MICRO-SCALE CHEMICAL EFFECTS OF LOW TEMPERATURE WEATHERING OF DSDP BASALTIC GLASSES

by

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ABSTRACT

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Iris Blanche Ailin-Pyzik, Doctor of Philosophy, 1979

Dissertation directed by: Dr. Sheldon E. Sommer
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Unaltered deep-sea basaltic glasses are believed to be the best record of initial magma composition, and as such are important in the study of petrogenesis. However, these glasses are altered by their long contact with seawater, becoming hydrated and undergoing chemical exchange. This chemical exchange affects the composition of seawater and plays a role in the chemical equilibrium of the oceans.

A study of the trace metal and major element alteration of glasses from Deep Sea Drilling Project Site 396B has been conducted, using a selected area x-ray fluorescence technique (developed for this study) for the trace metal analyses, and the electron microprobe for the major elements. The samples included sections of pillow basalt rinds, hyaloclastites, and a few crystalline sections.

The glasses were found to release about one-half the original Si and Al, two-thirds of the Mg and Na, and

over 90% of the Ca originally present, during alteration to palagonite. Fe and Ti were found to be immobile, and K was increased 40-fold by concentration from seawater. For the trace metals, over one-quarter of the Zn, Cu and Ni were released, 40% of the Mn, and over 10% of the Cr. These changes apply only to the conversion of fresh glass (sideromelane) to palagonite (smectite), and do not include the effects of authigenic phillipsite and calcite reprecipitated locally. Differences between the effects of low temperature weathering on the crystalline basalts and the glasses appear to be primarily a function of the susceptibility of the primary mineral phases to attack, with the glass, being the least stable phase, being the most altered.

There is something fascinating about science.
One gets such wholesale returns of conjecture
out of such a trifling investment of fact.

Mark Twain, Life on the Mississippi, 1874

to my father, of blessed memory, and my mother

David and Pauline Ailin

and my husband

Albert John Pyzik

in gratitude

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List of Abbreviations and Terms

DSDP - Deep Sea Drilling Project

EMP - electron microprobe

XMP - x-ray milliprobe

ZAF - abbreviation for electron microprobe correction procedure including terms for atomic number (Z), absorption (A), and fluorescence (F)

sideromelane - generic term for fresh, unaltered glass

smectite - expandable clay product of alteration of glass, including montmorillonite

palagonite - generic term for altered glass

phillipsite - zeolite mineral of general formula $(K_2,Na_2,Ca)(Al_2Si_4)O_{12}\cdot 4.5H_2O$

FeO - total Fe as oxide

INTRODUCTION

Basaltic glasses are believed to be the best representation of erupted magmatic composition, due to their quick cooling and relative resistance to alteration (Langmuir et al., 1977). However, they are hydrated and altered during contact with seawater, giving rise to alteration crusts of varying thicknesses and compositions, termed palagonite (Moore, 1966). There is considerable controversy concerning the conditions under which this alteration takes place (Bonatti, 1965). The study of basalt petrogenesis is hampered by the alteration of these glasses, particularly since alteration may proceed along microstructural fractures into the interior of the basalt, before intermediate areas are affected, and thus alter the composition and fabric of the glass (Hekinian and Hoffert, 1975).

The glass phase is thermodynamically unstable, and with time will eventually crystallize. When water is absent, this process is similar to the crystallization of silicate melts. In the presence of water, as in the case of marine basalts, devitrification will occur along fractures where exposure to water occurs (Marshall, 1961; Bonatti, 1965). The water acts by leaching cations and forming hydroxyl groups with silica. The removed species may be transported

long distances or may be redeposited locally as authigenic minerals and cements.

The alteration of crystalline basalt and basaltic glass may have a major affect on the overall composition of seawater, since erupted basalt covers a large portion of the oceanic floor, and may in fact be the major control of seawater concentrations for some elements (R.A. Hart, 1973; Thompson, 1973). The importance of this alteration process is in part a function of the large amount of material available to be altered. Contact with seawater is required, and is provided even at significant depths by movement along fault zones, brecciated zones, cooling joints and grain boundaries. The conversion of dark, fresh, basaltic glass (sideromelane) to palagonite (more properly, palagonitized glass) is greatly abetted by the increased flux of seawater. Removed species may be flushed out to remain in solution or be deposited elsewhere, or be locally redeposited as alteration products. The alteration products themselves are more permeable than the parent basalt, and thereby provide new pathways for alteration. The correlation of time (as distance from mid-oceanic ridge spreading centers) and progressive alteration of basalt has been demonstrated (Moore, 1966; R.A. Hart, 1970; Hekinian, 1971), and the similarity of the trends traveling away from the ridges to the interior to exterior tends found in altered pillows.

Bulk compositions of basalts may be determined, but of course cannot differentiate altered and unaltered material where alteration crusts are on the order of hundreds of micrometers. Bulk composition data requires a limiting assumption, which is usually the upper limit of water content, to distinguish between altered and unaltered basalts (S.R. Hart, 1969; R.A. Hart, 1970). Where zones are large enough to be separated by cutting, appearance may be the determining factor (S.R. Hart et al., 1974). Ideally, the analysis of a small area of a sample would be carried out without grinding up the sample, or destruction of the analyzed areas. Electron microprobe analysis may reduce this problem of combining of fresh and altered portions, but causes the decomposition of hydrous materials and mobilization and loss of alkali metals under beam loading (Scott, 1971; Scott and Hajash, 1976; Butt and Vigers, 1977). Also, it cannot easily be used to determine trace element composition when the concentration is less than about 100 ppm, due to the effects of electron beam-sample interaction, and the higher background resulting from higher excitation voltages, although this will vary with analyte and sample matrix.

Analysis of small areas of solid samples may be performed by other techniques, such as laser optical emission, ion microprobe, energy dispersive systems attached to a scanning electron microscope (SEM), and selected area x-ray

fluorescence. The first two techniques are not commonly available, and present problems with standardization and trace element analysis. Energy dispersive analysis using an SEM suffers from both the limitations of energy-dispersive systems (spectral overlap and long counting times for trace analysis) and those of primary excitation (high background). Selected area x-ray fluorescence has the advantages of both crystal dispersion (less spectral overlap) and primary excitation (lower background), and although it too requires relatively long counting times, most importantly, sample damage is not a problem as with the electron microprobe.

Studies of basalt petrogenesis utilize trace element information to help define fractionation trends (Nesbitt and Sun, 1976; Haskin and Korotev, 1977; Ridley et al., 1977) as well as major element data (Hekinian and Thompson, 1976; Pearce et al., 1977). It is necessary for these studies to have analyses of the freshest possible material, and to be able to distinguish between fresh and altered glasses (Noble, 1967). It is also necessary to have both types of data available for the same samples in order to evaluate the overall effects of alteration of basaltic glasses by interaction with seawater.

This Project

This study is an attempt to provide both major element and trace elemental data on altered and unaltered glasses from Deep Sea Drilling Project (DSDP) Leg 46, Core 396B, in such a manner as to avoid destruction of the sample during analysis, and to provide for the best possible distinction between altered and unaltered material during analysis. To this end, the electron microprobe (EMP) and x-ray milliprobe (XMP) have been utilized; the first to provide major element analyses, and the second for trace metals.

The effects of alteration on major and trace element composition may be examined using paired data for fresh and altered glasses in individual samples. Total iron will be used as the main indicator of degree of alteration, since it has been shown to vary directly with the degrees of oxidation and hydration, and to be immobile under the conditions which have prevailed during the alteration of these basalts (Honnorez et al., 1978; Bohlke, 1978). Trace element changes will also be keyed to total iron, via the milliprobe analyses. For a few crystalline samples to be examined, traverses across varying areas will be used to examine the use of this technique in studying elemental changes with crystal morphology.

This is the first attempt to determine trace elements

on intact samples, thus retaining the spatial relationship of fresh and altered material. Such analyses should yield essential information on the distribution of trace metals as effected by the alteration of the glass phase.

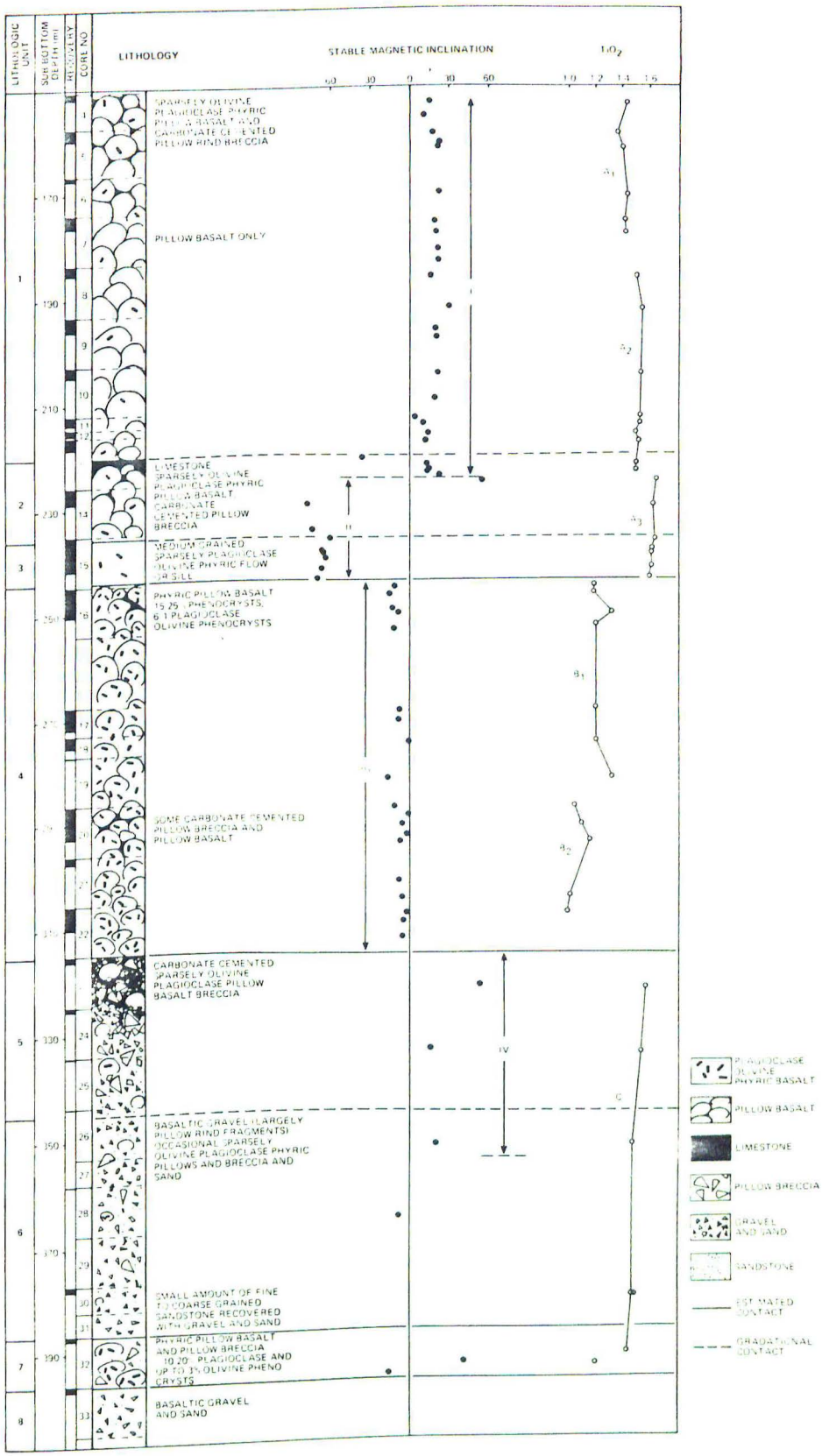
SAMPLING SITE

The Deep Sea Drilling Project (DSDP) samples for this study were provided through Dr. Jose Honnorez of the Rosenstiel School of Marine and Atmospheric Sciences of the University of Miami, as part of a joint University of Maryland-University of Miami grant from the National Science Foundation. The samples were obtained as sections from Site 396B, Leg 46 of the DSDP. This site was drilled in February 1976 in the Atlantic Ocean at $22^{o}59'N$, $43^{o}31'W$ in 4465 meters of water. 255.0 m of basaltic basement was drilled beneath 150.5 m of sediment. The site was located about 150 km east of the axis of the Mid-Atlantic Ridge (MAR) and dated as 9 m.y. old by its location in magnetic anomaly 5, and 13 m.y. old by fossil dating (Dmitriev and Hiertzler et al., 1978). DSDP sample numbers used in this study are of the form: core # - section # - piece #, sometimes with (cm from the top of the section) or (subsample number). Core sections were 1.5 m long. (Letters after the sample number generally indicate that an attempt was made to prepare more than one section of the sample for this study, although in some cases only one may have been analyzed.)

Figure 1 from Dmitriev and Heirtzler et al. (1978) shows the depth, form, and fractional recovery of the cores

Figure 1. Stratigraphic column, Hole 396B.

(Dmitriev, Heirtzler et al., 1978)


LITHOLOGIC UNIT
SUB-BOTTOM DEPTH (m)
RECOVERY
CORE NO.
LITHOLOGY
STABLE MAGNETIC INCLINATION
I_{O_2}
SPARSELY OLIVINE PLAGIOCLASE PHYRIC PILLOW BASALT AND CARBONATE CEMENTED PILLOW RIND BRECCIA
PILLOW BASALT ONLY
LIMESTONE SPARSELY OLIVINE PLAGIOCLASE PHYRIC PILLOW BASALT CARBONATE CEMENTED PILLOW BRECCIA
MEDIUM GRAINED SPARSELY PLAGIOCLASE OLIVINE PHYRIC FLOW OR SILL
PHYRIC PILLOW BASALT 15-25 % PHENOCRYSTS; 6:1 PLAGIOCLASE OLIVINE PHENOCRYSTS
SOME CARBONATE CEMENTED PILLOW BRECCIA AND PILLOW BASALT
CARBONATE CEMENTED SPARSELY OLIVINE PLAGIOCLASE PILLOW BASALT BRECCIA
BASALTIC GRAVEL (LARGELY PILLOW RIND FRAGMENTS) OCCASIONAL SPARSELY OLIVINE PLAGIOCLASE PHYRIC PILLOWS AND BRECCIA AND SAND
SMALL AMOUNT OF FINE TO COARSE GRAINED SANDSTONE RECOVERED WITH GRAVEL AND SAND
PHYRIC PILLOW BASALT AND PILLOW BRECCIA 10-20 % PLAGIOCLASE AND UP TO 3% OLIVINE PHENOCRYSTS
BASALTIC GRAVEL AND SAND
PLAGIOCLASE OLIVINE PHYRIC BASALT
PILLOW BASALT
LIMESTONE
PILLOW BRECCIA
GRAVEL AND SAND
SANDSTONE
ESTIMATED CONTACT
GRADATIONAL CONTACT

at the site. Further details on this site as well as the initial reports of the principal investigators may be found in Dmitriev and Heirtzler et al. (1978).

Comprehensive studies of the alteration of crystalline basalts from this site are reported in Honnorez et al. (1978) and Bohlke (1978). In general, they found evidence of early non-oxidizing alteration, followed by oxidative alteration. Alteration in the crystalline brown zones was found to have no effect on Ti, Al, Fe, Ca and Na, although an increase in bulk density of 10% makes them appear to have increased. Ca and Na were retained by the most altered crystalline rocks, though lost by glasses. Mg, Co and Ni were found to have been lost. Their results will be further discussed with the results from this study.

PREVIOUS WORK

A note on terminology:

The meaning of terms used to describe fresh and altered basaltic glasses varies with use by different authors. Although the terms altered glass, palagonite and smectite are used to refer to the same material, an individual author will generally use one term consistently. The term smectite is used because it implies the identification of the phase as being an expandable clay (montmorillonite). When discussing the work of others, their terms have been retained. When discussing the removal or addition of elemental species, however, the specie has been reported here in its elemental form, rather than as oxide or ionic species in solution, regardless of the form used in the original publication.

Pillow lavas generally have the form that their name suggests - elliptical sack-like sections of a basalt flow. Some pillows are connected by necks, indicating a rupture of an earlier flow to allow the formation of the next pillow. Moore (1975) reported the first direct observation of the formation of pillow lava during the eruption of Kilauea. Pillows were not actually formed - rather being elongated

tubes whose crusts were cooled in contact with water. The crusts of the tubes were broken by the force of lava flowing into the lobe, and growth then continued by lobes growing from these cracks.

Pillows may form from hot subaerially extruded lava dripping into water, but in the case of the deep-sea basalts must have been extruded under water. One of their most striking features is the radial jointing of their glassy crust; roughly hexagonal cracking of the glassy crust may result from shrinkage on cooling (Hess, 1967). It is the glasses formed during the quenching of these pillows that are of such interest to geochemists and volcanologists, being the rapidly quenched record of original magmatic composition. It is also these glasses and their alteration that are of primary interest in this study.

During the cooling of the pillow rinds, small fragments break off and accumulate around the cooling pillows. 'Hyaloclastites' are breccias formed from these granulated fragments. They are commonly masssive, showing no stratification or sorting, and are cemented by interstitial zeolites and/or calcite (Hess, 1967). It is in the hyaloclastites that the greatest opportunity for alteration of the glass fragments occurs, since the fragments are surrounded by cracks and crevices that permit the free flow of water (Furnes, 1974; Honnorez, 1978).

The degree of alteration of basaltic glasses has been involved in the study of mantle composition, sea-floor spreading and sea-floor vulcanism, since the effects on glass composition interfere with the determination of original magma composition. In order to understand these processes the effects of alteration by seawater must be understood (S.R. Hart et al., 1974). Other studies focus on the other member in the alteration process - seawater - and the effects on oceanic chemical balances that may occur (Mackenzie and Garrels, 1966; R.A. Hart, 1973).

Major Elements

Moore (1966) measured thicknesses of palagonite layers in samples from dredge hauls of pillow basalts from Hawaiian volcanoes. He described palagonitization as proceeding inward from the outer surfaces of the pillows, and from cracks and fissures into the glass, as a diffusion process. Hydration was regarded as the first step in the alteration, followed by the exchange of some elements with seawater, and then followed by progressive devitrification and crystallization of the resulting minerals. The palagonitized glass in some cases was itself layered, appearing a light yellow immediately adjacent to the glass, and browner further from the fresh glass contact. Moore reported, from microprobe analyses, that exchange with seawater during this alteration

caused a loss of Na, Ca and Mn, and a gain of K, Ti and Fe. Moore also found that the rate of alteration was a function of the square root of time (increasing thickness of palagonite coating as a function of time), as is the rate of hydration of obsidian, although the rates are much slower for the subaerial hydration of obsidian that was used for comparison.

The thickness of palagonite rinds in hyaloclastites, however, may not be a good measure of the age of the material. Furnes (1974) observed in hyaloclastites from Iceland and the Azores that complete filling of vesicles by palagonite and authigenic minerals may occur following some degree of alteration of the glass fragments. This would in turn reduce the access of the altering fluid (seawater) and perhaps cause further alteration to be impossible. Thus the thickness of the alteration crusts would no longer be a function of the time of exposure.

Palagonitized tuffs off Hawaii were the subject of a study by Hay and Iijima (1968). They concluded from microprobe studies of the sideromelane and palagonite that for equal unit volumes of these two materials, the sideromelane had lost approximately 1/3 of the Si, 1/2 of the Al, and 3/4 or more of the Ca, Na and K originally present in being converted to palagonite. They also indicated that the conversion of sideromelane to palagonite is essentially isovolumetric, based on primary textures being undistorted, and lack of shrinkage or expansion cracks in palagonite tuffs

and the enclosing fresh tuff respectively. The specific gravity of fresh glass was reported as 2.78, with palagonite varying from 1.93-2.10. The surprising lack of volume change indicates that a more open-structured phase is being formed with individual species being removed, but without total collapse of the rest of the structure. The fractional changes reported were calculated by assuming isovolumetric alteration and using the specific gravities mentioned above. The loss of elements, in other words, is not displayed by a volume change, but by the change in density. Diffractometer studies showed poorly crystalline montmorillonite in the palagonite.

In their studies of zeolitic tuffs, the authors (Ibid.) found that phillipsite was the first zeolite formed, followed by others in a particular sequence. They believe that palagonite is not formed during quenching, but by percolation of cold ground water over periods of time. Studies of subaerial palagonitization are of importance in establishing the potential for alteration of sideromelane at non-hydrothermal temperatures, although the alteration is effected by fresh ground water, as opposed to seawater in marine conditions.

Other studies of subaerial alteration of basaltic glasses were those of Furnes (1978) and Lipman (1965). Furnes (1978) reported from a study of subglacial hyaloclastites in Iceland, that all major oxides were lost during alteration. Lipman (1965) compared the glassy and crystalline portions of basalts from Nevada. He reported that the

glasses showed less oxidation of Fe, higher water content, higher Al, and lower Si and Na, than their crystalline counterparts.

To study the rate of palagonitization of sideromelane, Furnes (1975) experimentally altered synthetic glasses. Starting with an alkali basalt, an olivine tholeiite, and a basaltic andesite, Furnes prepared synthetic glass disks with a central hole, and exposed each type of glass to seawater and deionized water in sealed pyrex capsules at temperatures from 20-90^{o}C for periods of time from 3.5 to 14 months. The growth of palagonite at the drilled holes was then measured. Measurable growth was found even in the case of those samples held at 20^{o}C for only 6 months. At 90^{o}C, only 3.5 months exposure was required for measurable thickness. Moore's (1966) results generally agree, in that his alteration rates for approximately 2-6^{o}C were lower than Furnes' for 20^{o}C. However, if Furnes' conclusion that alteration occurs immediately after extrusion even with short term contact at slightly elevated temperatures is correct, then Moore's measurements would have to include the combined result of both very low (2-6^{o}C) and moderate (20^{o}C) temperature alteration conditions, even on fairly young material. The extrusion of hot lava would locally warm seawater, causing initial alteration to proceed rapidly, and providing cracks and microfissures for later lower temperature alteration pathways (Scott and Hajash, 1976).

The rate of palagonite formation and manganese coating of basalts in a rift valley was examined by Hekinian and Hoffert (1975). A linear correlation was found between the thicknesses of the two types of coatings, indicating the progression of the alteration with age. Other alteration products reported included traces of chlorite, poorly crystalline montmorillonite, serpentine, smectite and halloysite.

Authigenic phillipsites, smectites and Fe-Mn oxides have been reported by Honnorez (1978) to be the principal products of submarine low temperature alteration of basaltic glasses. The formation of these minerals reflects the overall chemical alteration budget in that Ca has been lost from the final products and not retained in the authigenic minerals mentioned above. K, Na and Mn are enriched - the first two trapped from seawater by phillipsite formation, and the Mn as the oxide. Overall, Si, Al and Fe levels were found to remain constant. Mg, found to be enriched at the start of halmyrolysis was eventually lost, as Si was tied up in phillipsites and therefore unavailable for clay formation to trap Mg.

S.R. Hart et al. (1974) compared x-ray fluorescence analyses of unaltered cores and altered margins of basalts (distinguished by inspection), as well as the results of wet analyses for Fe(II) and Fe(III). The data yielded good agreement on direction of alteration for some species, (increases with alteration of Fe(III), Mn, K and H_2O, losses

of Si, Fe(II), Ti and Al) and disagreement on others (Na, P and Mg). The enrichment of K with alteration is generally confirmed by most studies including another by S.R. Hart (1969) on K/Rb and K/Cs ratios.

R.A. Hart (1970), using literature data for 112 deep sea basalts, found that the age of ridge basalts, determined by distance from the ridge, was also described by the increasing degree of hydration of the material. When hydrated, these rocks were found to undergo chemical exchange with seawater, releasing Si, Ca and Mg, and gaining in total Fe, Ti, Mn, Na and K. His results for direction of change with alteration agree roughly with those of S.R. Hart et al. (1974) but disagree on the matters of Ti and P. Both studies found no essential exchange of Al.

In discussing the long term buffering of the oceans, Maynard (1976) used literature values to evaluate the possible seawater-basalt exchange reactions. Although he considered low-temperature alteration, he believed refluxing of seawater in the high heat-flow areas near the ridges to be more important, expecially for Mg, K and Na, than low-temperature alteration processes.

R.A. Hart (1973) developed a model for exchange in the basalt-seawater system involving extensive alteration of the basalts and exchange with seawater. In this model, a combination of processes are utilized, which could abstract most of the stream input of K, Mg and Na and add Si, Ca,

Fe(III) and Mn in amounts comparable to stream input.

Trace Elements

Most of the studies thus far described have dealt primarily with major element composition. Trace element data in the study of basalt alteration is less widely described, especially for glasses as opposed to crystalline basalts, although some petrogenetic studies report trace metal data. Hekinian and Thompson (1976) used trace element analyses to help distinguish volcanic material from different sources. Others have used trace element data to study magmatic fractionation (McCarthy and Hasty, 1976; Nesbitt and Sun, 1976; Haskin and Korotev, 1977). Pearce and Cann (1973) also used trace element data to determined the magma sources of various basalts. Much trace element data in the literature appears as part of bulk analyses, but is not related to alteration. For example, Kempe (1974) reports trace metal data for some DSDP Leg 26 samples, but is concerned with petrogenesis, not alteration and does not discuss changes attributable to alteration; Rhodes (1974) is likewise concerned with Leg 9.

In Furnes (1978) study of a subglacial hyaloclastite in Iceland, Cr, Co, Cu and Ni were found to be consistantly higher in palagonite than in the parent, and V, Nb, Zr, Ce, Nd and La showed depletion. Variable results were found for Zn, Rb, Sr, Y and Ba with the least affected elements being Zn, Ni, Y, Ba and Nb.

R.A. Hart (1973), in developing the exchange model mentioned earlier, reported trace element data for a series of samples arranged in order of increasing alteration. The trends are toward decreasing Ni and Co, and increasing Cr and Cu with alteration. Al is reported to show no particular trend. Thompson (1973) however, reported inconsistent trends for Cr and Ni, and disputed Hekinians's (1971) conclusion that progressive alteration of basalt with distance from a spreading center follows the same pattern as inner core to outer margin variations. Thompson reported the inner-to-outer sequence in pillows to be from altered crystalline core to unaltered glass to altered glass.

Over the course of studies of the alteration of basalts and basaltic glasses, a fundamental argument has recurred over whether the alteration of sideromelane to palagonite is the result of alteration under hydrothermal conditions or of low temperature alteration. Opinions run the full range, for example, from that of Moore (1966) of long term hydration, to that of Bonatti (1965), that basaltic glass is hydrated and converted to palagonite immediately after eruption and exposure to seawater.

Studies designed to examine the effects of hydrothermal alteration require the selection of samples from areas with the requisite conditions, such as the median valley of the MAR (Humphris and Thompson, 1978a and 1978b), so that there has been no opportunity for low temperature

alteration to occur. Most synthetic studies (Furnes, 1975; Mottl and Holland, 1978) use reaction conditions closer to hydrothermal conditions (high pressure and temperature) than to low temperature alteration conditions. These studies may not provide redox conditions consistent with the increase in oxidized iron found with alteration (Bohlke, 1978; Honnorez et al., 1978; Seyfried et al., 1978).

Humphris and Thompson (1978a;1978b) chose samples of basalts dredged only from the median valley of the MAR, in order to obtain samples principally hydrothermally altered, and minimize the effects of subsequent low temperature weathering. In the major element studies of these basalts, they observed that Si was generally leached from the basalt, although a considerable amount might be reprecipitated in the form of other minerals. Ca was observed to be released on approximately a 1:1 molar basis with the uptake of Mg. Na and K trends were found to be variable. Major element fluxes were normalized to constant Al, and rims compared to cores, since little change in Al concentration was observed, and that was attributed to changes in other elements. The authors remark that normalization to Ti gives essentially the same results, although that element shows evidence of slight mobilization during alteration. Trace element studies of these samples indicated that B and Li are taken up, Be is not greatly affected, and Mn is mobilized, although wide variabilities in concentrations existed. Co, Cr, and Ni generally

showed little change in this study, although variations in some cases suggested redeposition as sulfides. Cu and Zn generally showed the same results as the other trace metals. Precipitation of sulfides in veins was observed, but not on a very large scale.

In a synthetic alteration study, Mottl and Holland (1978) reacted powdered fresh mid-oceanic ridge (MOR) basalt with seawater and an artificial Na-K-Ca-Cl solution at elevated temperatures (200-500^{o}C) and pressures (500-1000 bars). Times of 2-20 months were used to allow most elements to approach steady state concentrations in the solutions, resulting in solutions similar to geothermal brines. Net transfer resulted in incorporation of Na into solid sodic feldspar and analcime. Sr results were inconclusive. Si, Ca, K, Ba, B and CO_2 were leached into solution. Mg was transferred into the solid, with this transfer largely balanced by that of Ca into solution. At low rock:water ratios, two exchanges were found: Mg for Ca, and Na for Ca. The conditions used in this study are similar to those of Mottl et al.(1974), in which Fe was reported to be leached into the solution. This is inconsistent with other workers findings in actual samples of increased total iron (and increased Fe(III)) in the solid phase (i.e. Bonatti, 1965; Bohlke, 1978), and indicates that the redox conditions, at least, are not those under which the alteration at low temperatures is taking place.

R.A. Hart (1973) suggested that the principal altera-

tion products of basalts resulting from the action of seawater are K-rich smectite, chlorite (during metamorphism), and albite-actinolite (formed during greenschist metamorphism). The formation of the K-rich smectite has also been reported by Melson and Thompson (1972), as well as the effects of this change in adding K and H_2O while releasing Ca, Si, Na and Mn. They disagree, however, on the disposition of Mg. The formation of a K-rich smectite has also been reported by Seyfried et al. (1978), as a consequence of oxidative alteration, and by Honnorez (1978).

Various elemental ratios have been used to act as indicators of the extent of alteration. K/Rb and K/Cs ratios have been used, and were found by S.R. Hart (1969) to decrease during alteration of crystalline basalts, whether from low-grade metamorphism or exchange with seawater. The decreases in the ratios occurred in spite of a two-fold increase in K content, because Rb showed a five-fold, and Cs a twenty-fold enrichment.

The alteration of ridge tholeiites may lead to altered abyssal hill basalts with values of typical oceanic alkali basalts, as a result of seawater interaction. Hekinian (1971) studied these types of rocks from the East Pacific Rise and the Chilean Rise, and found that this could lead to erroneous rock type identifications. He found that fragments of pillow lavas showed three concentric zones - a light grey

core, a dark grey outer margin and an outermost reddish-brown margin. S.R. Hart (1969) reported similar zones. The light grey inner cores consist of holocrystalline rock. The dark grey zone is a margin with a variolitic texture. The reddish brown margin is described as highly altered and containing limonitic aggregates. Hekinian described this limonite as being abundant in the outer margins groundmass, and in veinlets and cracks. These rocks were analyzed to provide a differentiation between the core and the two outer margins, by cutting the sections before grinding. Ti was not found to show a detectable variation, nor did Si, Al, Ca and Na show a pattern of variation. Increased K and decreased Mg were found in the basin samples as opposed to those from the ridge provinces. It should be noted here that when bulk samples are analyzed, local mobilization and redeposition cannot be identified, and may be the case here for those elements for which no changes were found. In microcrystalline samples, even microprobe analyses may not be able to reliably analyze material in the very small interstices - especially if they are filled with hydrous clay minerals. Hekinian cites a characteristic of these altered basalts that indicates that they were altered by seawater weathering rather than by low-grade metamorphism or deuteric alteration; that is, that the unaltered phenocrysts of plagioclase and fresh micro-phenocrysts would have been altered along with the groundmass if deuteric or metamorphic processes were involved.

Frey et al. (1974) found that DSDP cores from Legs 2 and 3 consisted mainly of partly altered basalt, with some palagonite-free (unaltered) glass present. They observed that low temperature alteration of oceanic ridge basalts caused increases in B, Li, K, Rb, Cs, U, Fe(III)/Fe(II) and H_2O. The alteration of glass to palagonite was found to result in larger changes than the alteration of crystalline materials. The altered glass showed greater loss of Na, Ca, Mg, Mn and Si and greater enrichment of K, H_2O, total Fe and Fe(III). Trace elements also showed greater changes in the glass, although they are in the same direction; Pb, Cu, Ba, Sr, B, Li and Rb are reported to be enriched in the altered material, and Cr, Ni and V to be depleted. Co, Y, Zr, Hf and Sc showed little change. Thus they found that although the process of alteration results in greater changes in the glasses than in the crystalline basalts, the direction of change was the same in either case. The greater severity in the glass alteration is not unexpected, since the glass is the less stable phase (Marshall, 1961).

Hart et al. (1974) further examined previously studied samples (S.R. Hart, 1969) for the effects of alteration. Zn, Cr, Co, Y and Nb were found to exhibit no changes outside experimental error. Si, Al and Ca were found to be lost, and Fe(III), total Fe, Mn and K were found to increase. Other elements such as Mg, Na, P, Ba, Ni and Cu exhibited inconsistent changes. In this study, even initial alteration

was found to produce possible marked heterogeneity, and that extreme alteration might again 'homogenize' the rock.

Lawrence et al. (1975) reported on their studies of oxygen isotopes and major cation composition of pore water in DSDP cores, and discussed the implications of their results on theories of alteration. Their work showed decreases in $^{18}O/^{16}O$ with depth, as well as decreases of K and Mg, and increases in Ca in the pore waters. This indication of removal of ^{18}O, K and Mg from seawater, and addition of Ca constitutes evidence that the reaction of the basalts with seawater does indeed affect the concentrations of elements in seawater by reaction with many meters of basalt required to account for the observed ^{18}O depletion. This contradicts other work (Muehlenbachs and Clayton, 1972) suggesting that much less basalt is involved, and therefore could not include sufficient material to affect oceanic mass balances, although local reprecipitation reactions could serve to aid in the silicate buffering of the oceans.

Many of the studies reviewed here have been concerned with crystalline basalts, rather than basaltic glasses. The trend with alteration appears to be largely the same, (Bonatti, 1965; Moore, 1966; Frey et al., 1974) although the alteration of the glass is more severe. The minerals found associated with altered glasses, such as smectite, phillipsite and calcite, are a likely repository for some quantity of the released species. Many of the previous

studies disagree on the effects of alteration on the trace metals, even when they largely agree on major elemental changes (i.e. R.A. Hart, 1973; Thompson, 1973). This may be a function of different conditions for alteration, a factor that could vary from site to site in matters of duration of higher temperature exposure and original phase and composition of the basalt.

EXPERIMENTAL

The analysis of intact samples of fresh and altered glasses requires the ability to examine small (50-250 um) areas on a prepared section of a sample. The analysis of smaller areas allows for improved exclusion of undesired phases and the analysis of a solid section does not require cutting of the sample to remove the unwanted phases prior to grinding. The electron microprobe is the ideal tool for the analysis of major elements in small areas, but is hampered in the analysis of trace metals (50-100 ppm) by dehydration and destruction of the sample due to electron beam loading at the high excitation voltages and long counting times necessary. For major elements, at low specimen currents and with a defocussed beam, satisfactory results may be obtained with minimal sample destruction (Scott, 1971).

The secondary (x-ray) excitation used in the x-ray milliprobe does not result in sample destruction and dehydration as does the primary (electron) excitation used in the electron microprobe. Longer counting times can then be used to improve counting statistics and detection limits, while permitting the analysis of small (100-200 μm) areas for selected trace elements.

Sample Preparation

The sample sections obtained were chosen and cut with a small diamond saw to exhibit a face with materials in varying stages of alteration, such as fresh glass, altered glass, calcite or zeolite cement, and calcite or phillipsite veins. The sample was then mounted in a 1" OD bakelite ring with epoxy, and allowed to cure overnight. The surface was polished with SiC paper down to 600 mesh, and then down to .25 um diamond paste, as is the usual procedure for electron microprobe (EMP) samples. In some cases the polishing procedure may have destroyed a feature of interest - either by plucking or polishing it away. Another section was prepared if possible with the same feature. This points up one difficulty in working with polished sections as opposed to thin sections - the chance that the phase under analysis is not sufficiently thick for x-ray analysis to be confined to the one phase.

The solid section technique was chosen after the analsis of thin sections was attempted. The analysis of thin sections is possible by EMP, but attempts at x-ray milliprobe (XMP) analysis revealed that the depth of penetration (critical thickness) exceeded the thickness of the sections, thus yielding low results with solid standards. XMP analysis would therefore have required standards also prepared as

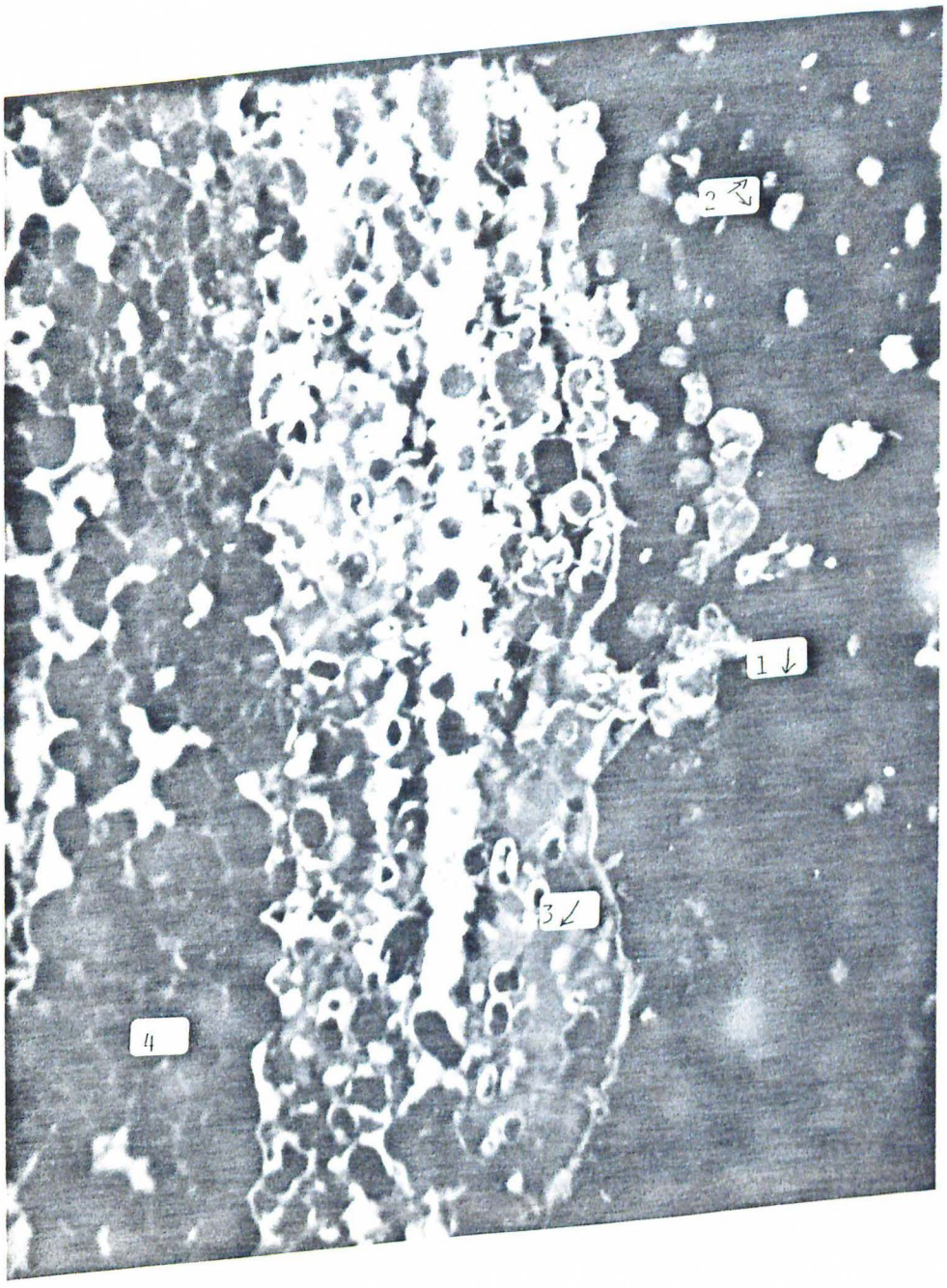
thin sections, thus making the thicknesses of the standards and samples a critical parameter.

In order to provide an initial position marker for the XMP analyses, two strips of adhesive backed Cu foil were applied to the surface of the sample, at right angles to each other, bracketing the areas of interest. Their use will be described later.

Figures 2 and 3 show two of the samples with different areas of interest identified. Fresh glass appears dark in solid section, with altered glass various shades of golden brown and darker brown. Varioles are areas of crystallization in the glass, and may remain when all the amorphous glass around them has been severly altered, since the glass is less stable than the crystalline phases. Some crystalline areas display remnant outlines of varioles defining the crystallization zones having grown from a single nucleation site. The microcrystalline basalts are generally very closely intergrown plagioclase laths. Phillipsite can generally be recognized in vein fillings by its fibro-radial habit, often with the remainder of the vein filled with a clear, glassy looking material, which shows very high Ca from microprobe analyses - presumably calcite.

Figure 2. Sample 6-1-1 (4-7) B

Figure 3. Sample 7-2-9 (97-102)



SAMPLE 6-1-1 (4-7) B

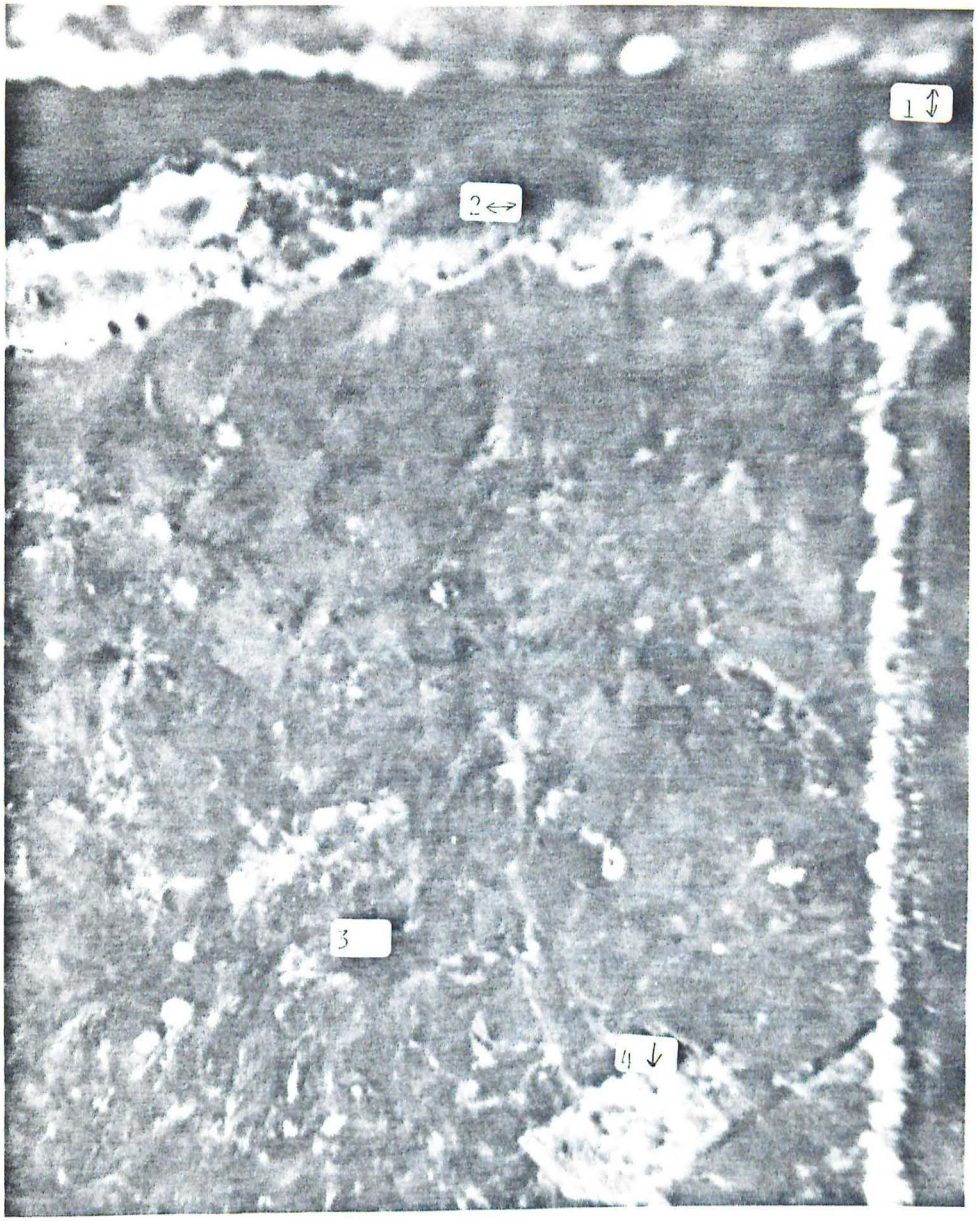
1) CLEAR GLASS (FRESH)

2) GLASS AND VARIOLES

3) ALTERED GLASS-'PALAGONITE'

4) VARIOLITIC AREA

Long dimension = 0.5 cm



SAMPLE 7-2-9 (97-102) A

1) FOIL STRIPS
2) PHILLIPSITE FILLED CRACK
3) CRYSTALLINE ROCK
4) OLIVINE INCLUSION

Long dimension = 0.6 cm

Electron Microprobe Analysis

The electron microprobe (EMP) uses an electron beam to excite x-radiation from a small sample volume. Unlike x-rays, electrons can be focussed to a small spot using electromagnetic fields. However, in this use of primary excitation (electron bombardment) an x-ray continuum is produced, that is not produced by x-ray bombardment, as in the x-ray milliprobe. The continuum contributes to a higher background, making trace analysis less efficient. The EMP however, is extremely useful for major element analysis, in the ability to analyze a very small spot. The electron beam - sample interaction may be severe, and the effects must be accounted for. In computerized systems, the corrections are usually incorporated into the control system.

In the present study, a Cambridge Microscan V Electron Microprobe with two crystal spectrometers was used for major element analyses. A peculiar characteristic of this particular instrument is the high take-off angle (angle of the electron beam to the x-ray paths to the spectrometers) of 75^{o}. This minimizes the path length of x-rays in the sample to reduce interaction of secondary x-rays with the sample, and minimizing the effects of differences in the carbon coatings of the standards and samples. Operating and counting

conditions used are shown in Table 1. The computerized control program used in this system incorporates ZAF corrections which are applied automatically to the analyses. The correction procedure was written in BASIC by Finger (1973), based on MAGIC IV by Colby (1971).

A fragment of the Kakanui horneblende was used as the EMP calibration standard. Table 2 shows the major element composition, along with calculated detection limits using the formula:

$$\text{detection limit} = 2\sigma = \frac{2\sqrt{2}}{m}\left(\frac{I_b}{T_b}\right)^{1/2}$$

m = counts/sec/concentration unit
I_b = background count rate
T_b = counting time

(Jenkins and deVries , 1978)

The Kakanui was analyzed as an unknown periodically during a days' operation, and the factor necessary to return to the total analysis percentage was used as a multiplier to correct the unknown analyses. This factor usually ranged between .99 and 1.10. Mn analyses by EMP were of lower quality than the other elements determined. This was due to the use of a second order peak, chosen to utilize the automation capacity fully, which allows for the use of only two crystals in the analysis sequence. Note that the calculated detection limit is generally higher than the sample levels.

The same samples were used for EMP and XMP analysis. Each sample was examined under a binocular microscope using

Table 1

Electron microprobe operating and counting conditions

Filament: 20 kV, approx. 100 μA

Specimen current: .02-.03 μA

Spot size: approx. 75 μm

Counting time: 10 sec. per peak or background measurement

Element	Crystal	Order	K_α($^{o}2\theta$)
Si	RAP	1	31.66
Al	RAP	1	37.23
Fe	PET	2	52.52
Mn	PET	2	57.42
Mg	RAP	1	44.50
Ca	PET	1	45.13
Na	RAP	1	54.25
K	PET	1	50.63
Ti	PET	1	36.62

PET 2d = 8.7500 Å RAP 2d = 26.130 Å

Gas flow proportional counter voltages

for elements by PET: 1160 V

for elements by RAP: 1240 V

Backgrounds taken at $+2^{o}2\theta$ for all elements but Na and K, taken at $+1^{o}2\theta$

K_α values from instrument operating manuals. Note that these are reference values, with peaks located by computer controlled standardization program

Table 2

Analysis of Kakanui horneblende and EMP detection limits

	% *	estimated analytical error **	detection limit ***
SiO_2	40.37	.05	.09
Al_2O_3	14.90	.12	.06
FeO	10.95	.26	.25
MgO	12.80	.14	.08
CaO	10.30	.15	.02
Na_2O	2.60	.17	.16
K_2O	2.05	.04	.01
TiO_2	4.38	.04	.02
MnO	.09		.34
H_2O^+	.90		
H_2O^-	.04		

*Analysis from Jarosewich (1972)

** Determined for operating conditions (Table 1) used in this study.

***Based on averages of repetitions on Kakanui horneblende.

Total Fe as FeO.

oblique lighting to show the various colors in solid section, and a petrographic microscope in the reflecting mode before being loaded into the EMP. In solid section samples, some features, such as varioles, are washed out in a reflected light system as is present in the EMP. Sites for analyses were selected using a sample site selection grid, although final choices were made using the optical system of the EMP. The data from these analyses is tabulated in Appendix A.

No evidence was found of Na loss during the time required for total analysis of a single spot at the counting conditions used, although such losses were reported by Scott (1971) for glass shards from ignimbrite cooling units. Scott used one-tenth the sample current, and one-tenth the spot size at 15 KV. Either the loss occurs in less than the initial two seconds of beam exposure in this study, or the large spot size and solid sample size assist in the dissipation of the heat generated by electron beam interaction. Scott did not indicate the water content of his samples or the overall sample size.

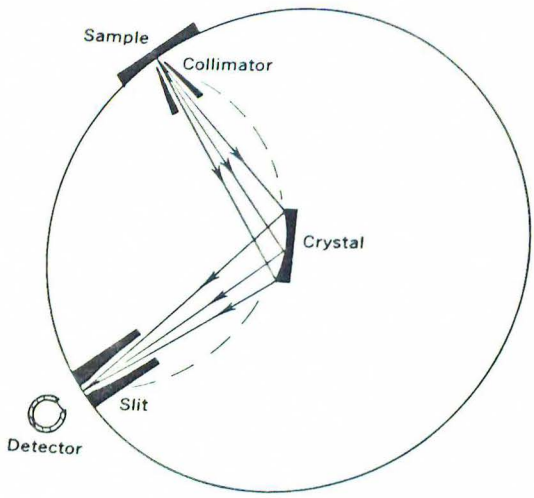
X-ray Milliprobe Analysis

The x-ray milliprobe (XMP) is a curved crystal x-ray fluorescence spectrometer with collimation of the secondary x-ray beam (Rose et al., 1969) (Figure 4). It is possible to collimate the primary beam at the x-ray tube window, to strike a small spot on the sample. However, this requires drilled lead plugs as the limiting aperture, and there is divergence of the beam before it strikes the sample. Secondary collimation allows selection of a small spot on the sample, and the lower overall energy of the beam allows the use of other aperture materials. This also helps to eliminate scatter from other parts of the instrument housing.

A conventional x-ray fluorescence (XRF) tube is used to irradiate the entire surface of the sample. An aluminum tube acts as the collimator between the sample and the analyzing crystal. For this study, a Pt SEM aperture (100 or 200 μm) was cemented onto the end of the relatively large (1500 μm) tube to act as the limiting aperture. Apertures ranging in size from 50 to 1500 μm were evaluated. The 100 and 200 μm apertures were selected as the most suitable for this work, given the areas of the fresh and altered glasses to be analyzed, and the 200 second counting time. Apertures smaller than 100 μm lead to unacceptable degradation of the detection limits at that counting time.

Figure 4. Secondary x-ray beam collimation

(Rose et al., 1969)



SECONDARY BEAM COLLIMATION

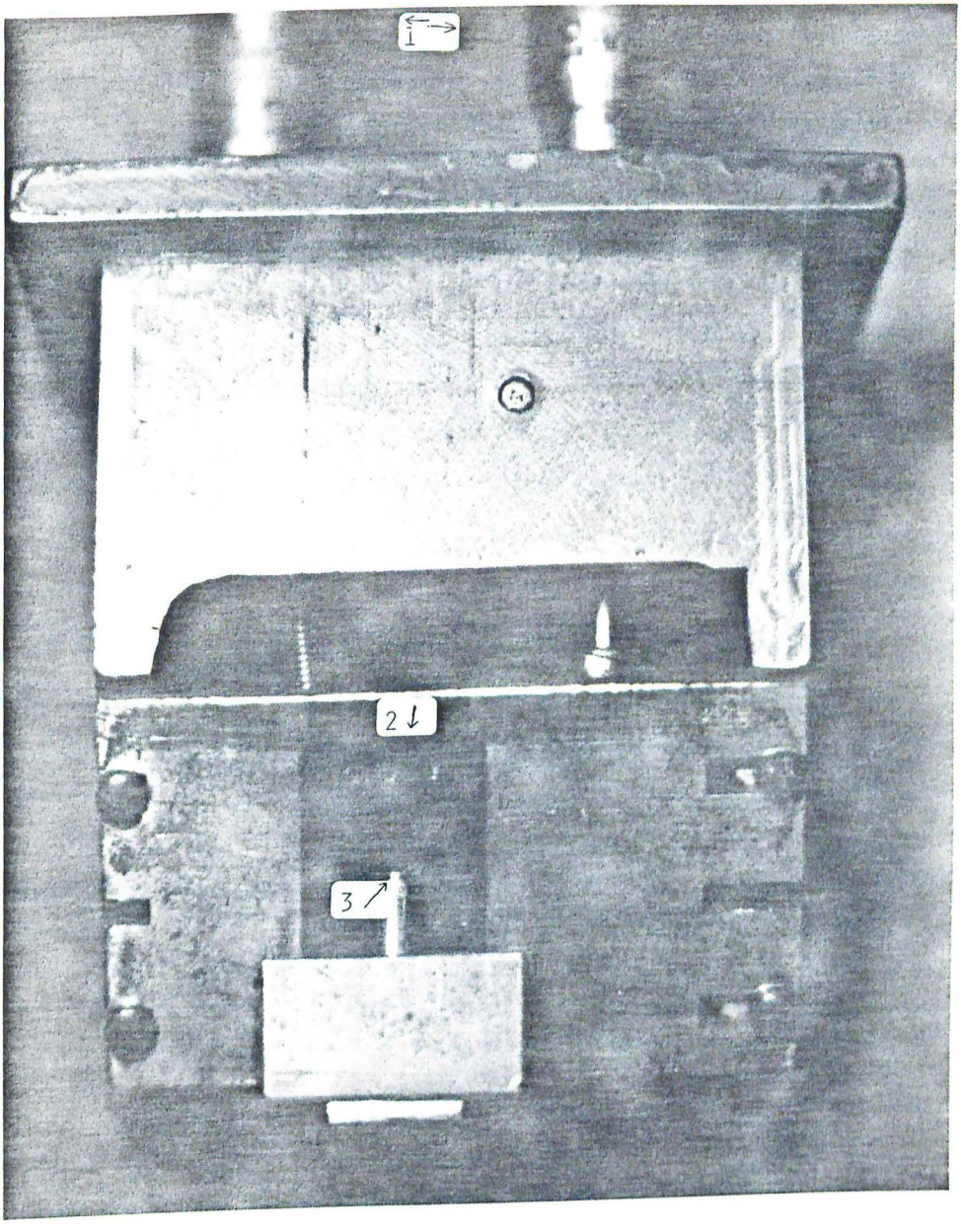
The Heinrich sample drawer with micrometer drives for sample positioning was used as the sample holder (Figure 5). The sample is held in place with a spring clip against the face plate of the holder. The use of the micrometer drives in sample positioning will be described later.

The entire x-ray path from the sample chamber to the detector was continually flushed with He gas to remove air and improve intensities. A two-detector system was used, consisting of a two-window flow proportional counter with a NaI scintillation detector in series after the flow counter (against the second window). Cr data was collected with only the flow counter, as the lower efficiency of the scintillation counter in that region resulted in its contributing little to the net peak. Operating conditions are shown in Table 3.

Standards for x-ray fluorescence should ideally be as similar as possible to the samples to be analyzed. However, glass trace element standards with 8-15% FeO are not readily available. In order to have glass standards with approximately this Fe content range, standards were prepared from analyzed basalts provided by Dr. E. Jarosewich of the Smithsonian Institution, and from USGS standard BCR-1, using a technique used for preparation of EMP samples (Smellie, 1972; Nichols, 1974). The use of other USGS standards was attempted, but good fusions could not be produced. The powdered basalt was placed in a tungsten boat and fused at 50 amps

Figure 5. Heinrich sample drawer

Oriented as seen by analyzer crystal



SAMPLE DRAWER

1) MICROMETER DRIVES

2) SAMPLE IN POSITION

3) SEM APERTURE ON COLLIMATOR

Table 3

X-ray milliprobe operating and counting conditions

X-ray tube: Pt target at 50 kV and 60 mA

Crystal: LiF 2d = 4.0267 Å
Radius of curvature = 14"

Detectors: Flow proportional counter with P-10 gas
1500 V

in series with

NaI scintillation detector
950 V

Voltages chosen to give approx. 3 V peaks

Analyzer windows: E_L = 1.0 V E_U = 5.0 V

Counting time: 200 sec. per peak or background measurement

	Kα reference ($^{o}2\theta$)*	Kα used ($^{o}2\theta$)	Background ($^{o}2\theta$)
Zn	41.80	41.45	43.45
Cu	45.03	44.50	46.50
Ni	48.66	48.08	50.08
Fe	57.52	57.00	59.00
Mn	62.97	62.60	64.60
Cr	69.35	69.12	68.12

*General Electric Co. (1966) X-Ray Wavelengths for Spectrometer

in an argon atmosphere until inspection showed complete fusion and disappearance of bubbles (approx. 10 seconds). The fused material was then removed from the boat, mounted in epoxy, and polished as were the samples. The homogeneity of the prepared standards was checked by electron microprobe for Ti, Mn and Fe. For these elements, point to point variation was less than the calculated analytical error for Ti and Mn, and about twice that for Fe. In determinations on the elements analyzed by milliprobe, the differences between standard concentrations recalculated from the calculated analytical curves were about 5% for Zn, 5% for FeO, 2% for Cu, 15% for Ni, 6% for Cr, and 0% for MnO to two decimal places. Compositions of the basalts used are shown in Table 4.

The standards were counted sequentially for the elements Zn, Cu, Ni, Fe, Mn and Cr, taking intensity measurements at the K_α peak locations, and at background locations approximately $2^\circ 2\theta$ higher, except for Cr. For Cr, background measurements were taken at $1^\circ 2\theta$ lower, to avoid the cutoff imposed by the limits of the curved crystal. Angles used and reference values for the K_α peak locations are shown in Table 3. The angles used were determined by slow scans of the elemental peaks on standards of higher concentration, and rechecking with a large (1500 μm) collimator on the standards being used.

Two spots on each standard were measured during each analysis sequence. The 200 second analysis time was the longest commensurate with counting 4 standards and 5-7 spots

Table 4

Composition of x-ray milliprobe standards

	USMNH 113154-D557	USMNH 113155-D613	USMNH 113155-D614	USMNH 113157-D823	USGS BCR-1
% SiO_2	49.51	51.03	50.35	49.93	54.48
Al_2O_3	16.26	13.28	14.36	14.80	13.65
FeO	8.99	14.06	12.20	11.59	12.15
MgO	9.01	5.02	6.86	7.53	3.28
CaO	12.30	9.37	10.95	11.17	6.95
Na_2O	2.20	2.48	2.35	2.22	3.31
K_2O	.14	.44	.19	.20	1.68
H_2O^+	.27	.86	.73	.48	.77
H_2O^-	.07	.20	.12	.07	.82
TiO_2	1.11	2.34	1.61	1.66	2.23
P_2O_5	.04	.17	.06	.04	.36
MnO	.16	.24	.22	.22	.17
ppm Zn	75	135	105	110	132
Cu	85	61	67	74	22
Ni	160	35	55	100	15
Cr	440	80	170	275	16

(cont.)

Table 4 (cont.)

Major element analyses of U.S. Museum of Natural History (USMNH) samples from Jarosewich (1977)

Trace element analyses of USMNH samples from Byerly (1977)

Analysis of U.S. Geological Survey (USGS) BCR-1 from Flanagan (1969)

Total Fe as FeO

per sample in a single day. To perform 12 counts per spot, (peak and background for each of 6 elements) for 2 spots on each standard, and 6 spots per sample required 11-12 hours. Initial determinations ccunting one spot on each standard befor the sample analysis and one after, showed no improvement or degradation of the quality of the data, but increased total analysis time, due tc increased sample handling and more He flushing time. Similarly, only one background count was taken, in order to halve the time required for background counting. Calculated detection limits using the same formula as for the EMP are shown in Table 5 for the two aperture sizes used. This table also shows approximate intensity ranges observed for each element and background.

To select locations for analysis on the samples, each sample was loaded into the Heinrich sample drawer, which is equipped with x-y motion controlling micrometer drives. The sample drawer was then placed on the stage of a binocular stereomicroscope (30-45x magnification). The position of the sample in the drawer was adjusted until one of the foil strips on its surface was parallel to the direction of travel of the upper micrometer drive (parallel to the axis of the micrometer drive handles), as seen by the line of travel of the eyepiece crosshair. This eliminated difficulties with the strips possibly not being exactly perpendicular to each other.

The Cu foil 'corner' location was then read and recorded, by bringing the crosshair to approximately one

Table 5

X-ray milliprobe detection limits and intensity ranges

	100 μm aperture		200 μm aperture	
	detection limit	counts/ 200 sec *	detection limit	counts/ 200 sec *
Zn	16 ppm	900-1200 750-800	1 ppm	18000-22000 1000-5000
Cu	3 ppm	1200-1600 550-650	1 ppm	5500-7000 600-900
Ni	42 ppm	550-650 400-600	10 ppm	700-2000 550-750
FeO	.04 %	14000-22000 600-800	.01 %	110000-220000 500-700
MnO	.04 %	350-500 ~300	.01 %	1200-2000 250-400
Cr	-		44 ppm	150-300 80-100

* First figure is peak intensity range, second is background intensity range.

aperture diameter from each foil strip in the 'corner'. Analysis sites were then chosen by driving the sample to bring a site under the crosshairs and recording the micrometer readings. Simple distance measurements on the surface of the sample would not be suitable, because the micrometer controlling travel parallel to the micrometer handles does not exert its force along the angled face plate of the sample drawer, but parallel to the handles. Analysis sites were chosen to provide 2-3 diameters surrounding of the same material to allow for positional error. The sample drawer was then loaded into the spectrometer and the Cu 'corner' located by the fall-off of Cu radiation as observed on the ratemeter. The relative x and y positions recorded using the microscope were then applied to the 'corner' position determined by the Cu radiation fall-off. The analysis was then performed on each spot as for the standards.

Redeterminations were made of the 'corner' position after the analysis was completed on a number of runs. Of ten such determination, the average repetition error was .14 mm (s.d.=.12) in the direction of motion parallel to the micrometer handles, and .05 mm (s.d.=.05) in the perpendicular direction. Although the actual spot size has not been determined, a calculation of the elongation along the slope of the sample drawer may be made. With the collimator oriented parallel to the bottom of the sample drawer, and the angle of the sample slope taken as 45^{o}, the major axis of the

resulting ellipse for the 100 μm aperture is (100 μm/sin 45° = 100/.71 =) 140 μm, and 282 μm for the 200 um aperture. Measurements of the distance between lines on a section of graph paper, made using the microscope and eyepiece crosshair with the paper mounted as a sample, indicate the actual angle to be close to 41°, thus making the ellipse dimensions 151 μm, and 303 μm. Thus the allowance of 2-3 aperture diameters clearance on each side of the chosen analysis site should be sufficient to allow for positional error and the elongation of the spot. The requirement of 2-3 aperture diameters area of the same material greatly restricts the choice of analysis sites, however. This is 200-300 μm in each direction for the 100 μm aperture, and twice that for the 200 μm aperture. Fresh glass fragments may be that large, but the choice of altered glass areas is narrowed considerably, since the alteration crusts are not as often of that size.

Data reduction was accomplished using the XRF-4 computer program (Marr, 1976a; Marr, 1976b). This program consists of a number of corrections routines that may be called after a single loading of peak, background and concentration data. The program package allows for various options such as eliminating a particular standard from the regression, subtracting backgrounds, or selection of one of the corrections procedures. The program was modified in the input and output statements only, to make it easier to enter the data, and to make it compatible with the version of BASIC in use

on the University of Maryland Computer Science Center UNIVAC 1108 computer that was used.

Since the FeO content of the standards ranged from 8-14%, and that of the samples was estimated to cover approximately the same range, the corrections available in the XRF-4 program were utilized in an attempt to evaluate the effect of the varying Fe concentrations, and to develop a correction factor. However, the use of XRF-4 yielded corrections for an Fe enhancement for Zn, Cu and Ni from such procedures as a linear correction model, and Rasberry-Heinrich procedure - not a reasonable result, considering the locations of the emission lines and absorption edges (Table 6). Since the data yielded acceptable calibration lines and regression coefficients using the XRF-4's uncorrected linear fit with backgrounds subtracted, and the regression line pegged at the origin, those calibrations were used. The program gives for each calculated curve a sigma value and an r value. Average sigma and r values are shown in Appendix C with the data tables, along with the required r values for 99% and 99.9% confidence limits.

The values of the sigmas and r values may be manipulated to some extent by eliminating standards from the regression calculation using a provision of the program. This may be carried to extremes by repeatedly eliminating the standard furthest from the line. A deviation in an individual measurement could be caused by a faulty count (caused by line

Table 6

Emission lines and absorption edges for XMP analyses

	Emission line (Å)	Absorption edge (Å)
Zn	1.437	1.283
Cu	1.542	1.380
Ni	1.659	1.488
Fe	1.937	1.743
Mn	2.103	1.896
Cr	2.291	2.070

(Bertin, 1970)

fluctuation or an error in goniometer position) or by systematic deviation of the concentration. However, this elimination was used only where a point was obviously out of line. In most cases no standards were eliminated from the regression calculation, with no more than two points eliminated in any single calculation.

Data for Cr determinations are presented in the tables only for those analysis runs made with the 200 μm aperture. The lower excitation efficiency of Pt for Cr, and the consequent lower intensities did not permit the calculation of satisfactory calibration curves for determinations made with the 100 μm aperture, where lower overall intensities were observed.

RESULTS AND DISCUSSION

Major Elements (Microprobe Analyses)

The results of microprobe analyses are summarized in Appendix A, with the organization of those tables explained in the Appendix. Appendix B contains calculations of the % change of the oxides, between fresh glass - altered glass pairs, based on analyses normalized to 100%, thus being a 'volatile free' weight basis. This would be similar to microprobe analyses on fused materials. 'Others' is the term used for the difference between the total microprobe analysis and 100%, constituting H_2O, CO_2 and any other variable such as pore space, i.e. density difference between standards and samples.

Microprobe analyses may also vary from 100% due to destruction of the sample during analysis. In the case of non-silicates however, such as calcite, the total analysis will not sum to 100%, but will show predominantly CaO. Destruction of the sample during analysis may result in a total of less than 100%, and may be a problem with hydrous materials. Thus 'others' is greater for the altered glasses than for the fresh glasses. In the analysis of the phillipsites however, although destruction of the sample was visible, many of the analyses neverthless sum to over 90%. It is possible in

these cases that the initial dehydration is so rapid that a 'fused' sample is then analyzed, resulting in high analysis totals.

Table 7 shows the results of least squares fits to the 43 data points in Appendix B, for each major oxide vs. % FeO. Table 8 shows further reduced averages for fresh and altered glasses from each core section. Two values are included for one core where the results for different fragments differed considerably. These data are plotted as fresh and altered pairs in Figures 6 to 12. The slopes of the equations in Table 7 constitute the average slope of the points plotted in these figures.

Fe, Ti and Al are reported to be passively accumulated, or immobile, during the oxidative alteration of the crystalline samples from these cores (Bohlke, 1978; Honnorez et al., 1978). Their apparent increases in altered materials are thus the result of the removal of other species. Humphris and Thompson (1978a) also report Al to be immobile. However, in the alteration of glasses where phillipsite formation is observed, mobilization of Al does occur (Honnorez, 1978), and it cannot be regarded as immobile. Ti and Fe may then be considered as immobile during alteration, since they remain while other elements are removed or added (Bohlke, 1978; Honnorez, 1978; Honnorez et al., 1978; Humphris and Thompson, 1978a). Fe has been used here for consistency, because it was also determined with the trace elements.

Table 7

Least squares fits of major oxides and FeO

			r	σ
% SiO_2	=	50.48 - .11 % FeO	.30	1.90
% Al_2O_3	=	16.54 + .03 % FeO	.10	1.98
% MgO	=	12.12 - .36 % FeO	.75	1.72
% CaO	=	20.22 - .97 % FeO	.94	1.79
% Na_2O	=	4.09 - .09 % FeO	.51	.78
% K_2O	=	- 3.10 + .35 % FeO	.96	.55
% TiO_2	=	.08 + .13 % FeO	.95	.22

43 points used

Table 8

Average normalized fresh and altered glass analyses

	4-1-4		4-2-3		5-2-1		5-2-4	
	FG	AG	FG	AG	FG	AG	FG	AG
SiO_2	49.76	50.51	49.97	51.02	49.31	48.11	50.35	48.80
Al_2O_3	17.61	17.68	16.16	16.97	15.40	20.82	16.49	20.01
FeO	7.10	18.29	9.58	18.26	9.27	19.38	9.74	17.08
MgO	9.72	4.58	5.70	3.55	8.73	3.24	8.47	3.65
CaO	9.87	.39	11.59	.75	12.85	.76	11.89	2.49
Na_2O	4.72	2.91	2.90	2.81	3.04	1.47	3.08	2.18
K_2O	.10	3.59	.10	4.19	.12	3.59	.11	3.49
TiO_2	1.01	2.03	1.26	2.31	1.35	2.57	1.26	2.32
Total	99.89	100.02	100.15	99.86	100.04	99.91	101.39	100.01

Table 8 (cont.)

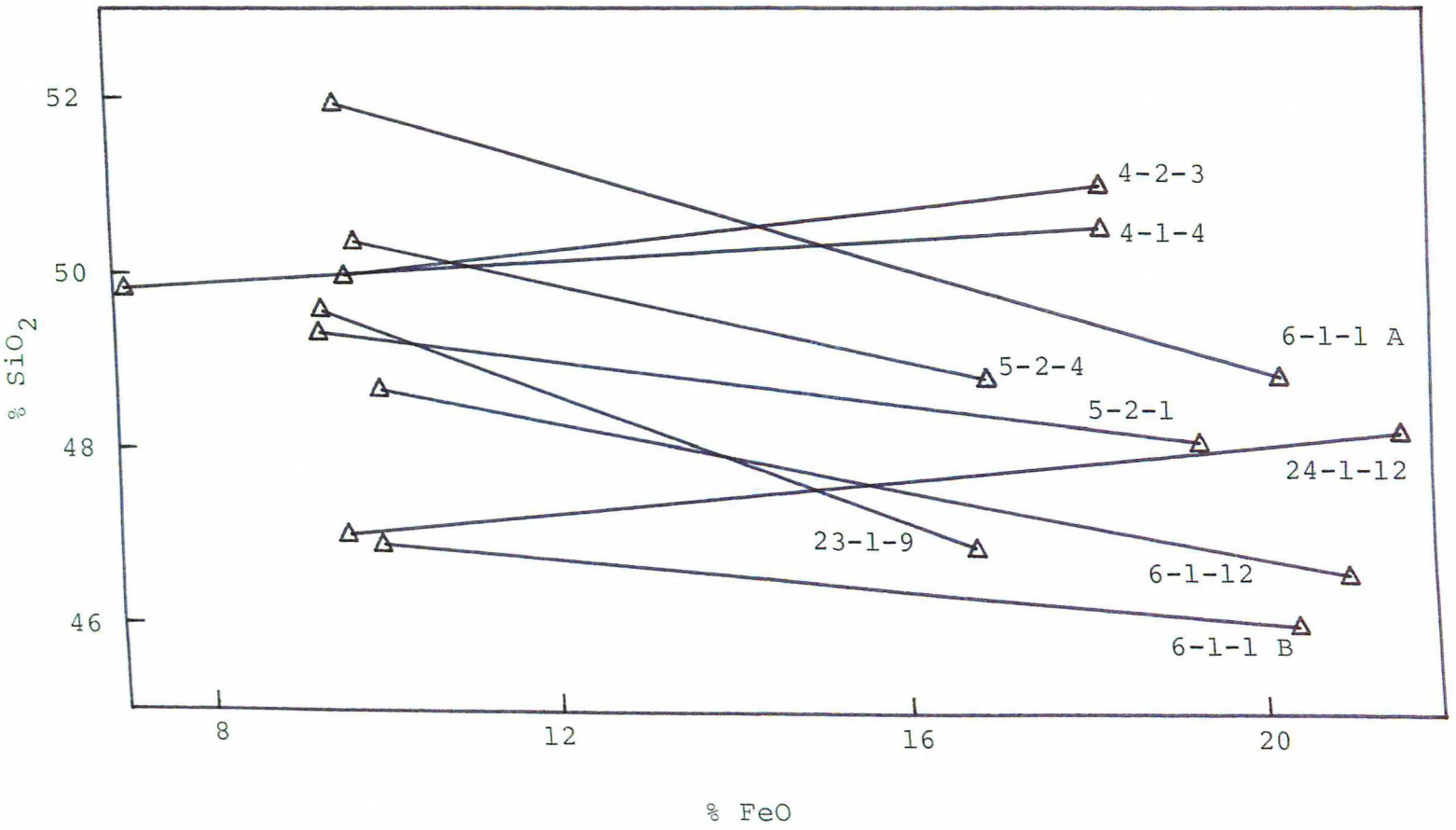
	6-1-1 A		6-1-1 B		6-1-12		23-1-9		24-1-12	
	FG	AG	FG	AG	FG	AG	FG	AG	FG	AG
SiO_2	51.87	48.87	46.92	45.99	48.64	46.60	49.51	46.91	47.00	48.21
Al_2O_3	15.99	17.80	16.79	16.54	16.23	17.80	17.07	15.58	16.78	13.42
FeO	9.55	20.31	10.03	20.39	10.08	21.03	9.34	16.78	9.63	21.66
MgO	8.36	3.81	9.59	9.44	9.01	4.15	8.12	9.74	8.82	5.43
CaO	10.16	.67	12.26	.68	11.64	.49	11.41	3.68	13.01	.60
Na_2O	2.76	2.38	2.82	1.14	2.97	2.66	3.22	2.79	3.37	2.67
K_2O	.10	3.56	.10	3.16	.12	4.77	.18	1.97	.17	4.57
TiO_2	1.24	2.66	1.56	2.43	1.26	2.78	1.38	2.47	1.42	3.32
Total	100.01	100.04	100.07	99.75	99.94	100.28	100.22	99.93	100.20	99.90

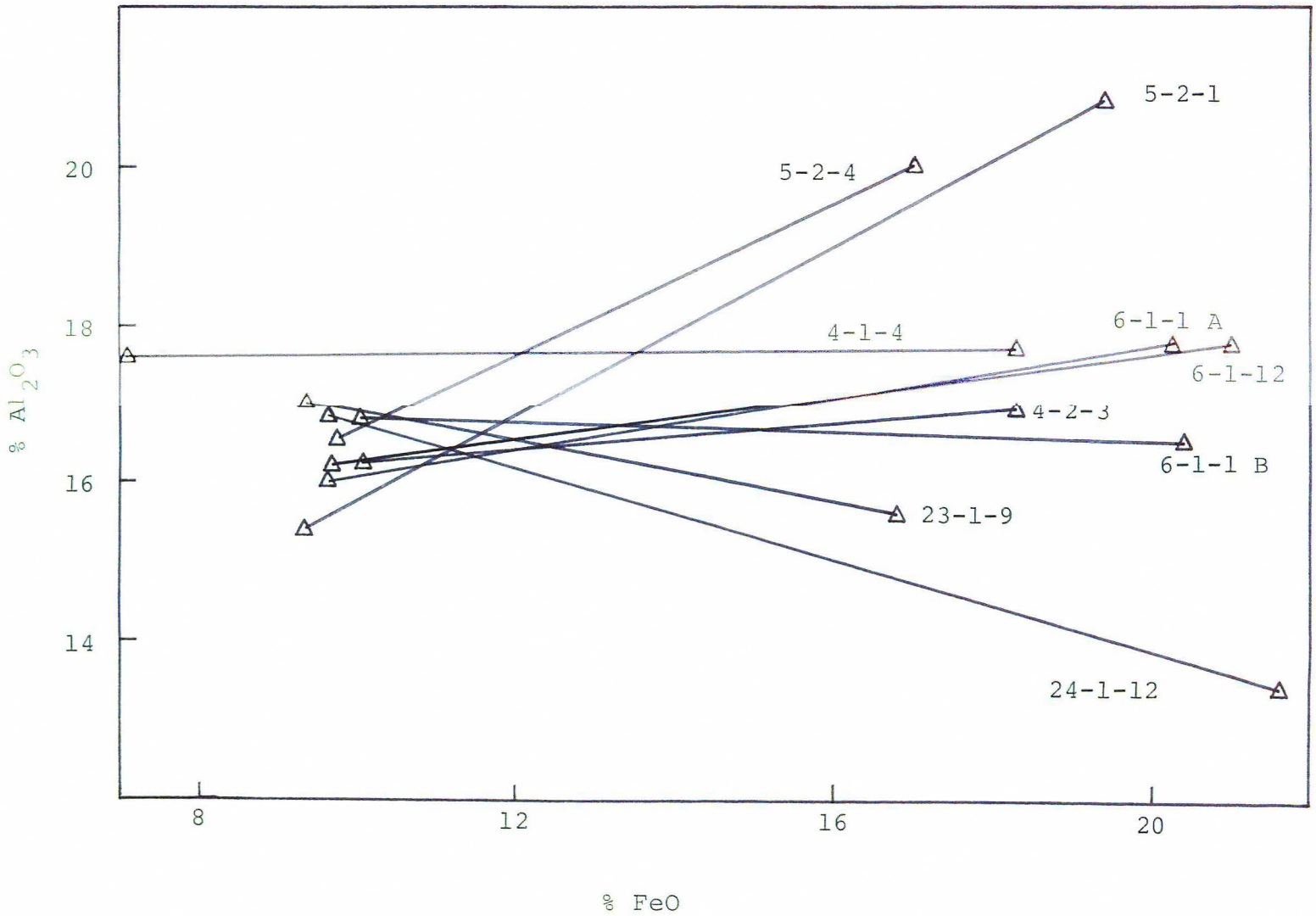
Plots of Normalized EMP FG - AG Pair Data

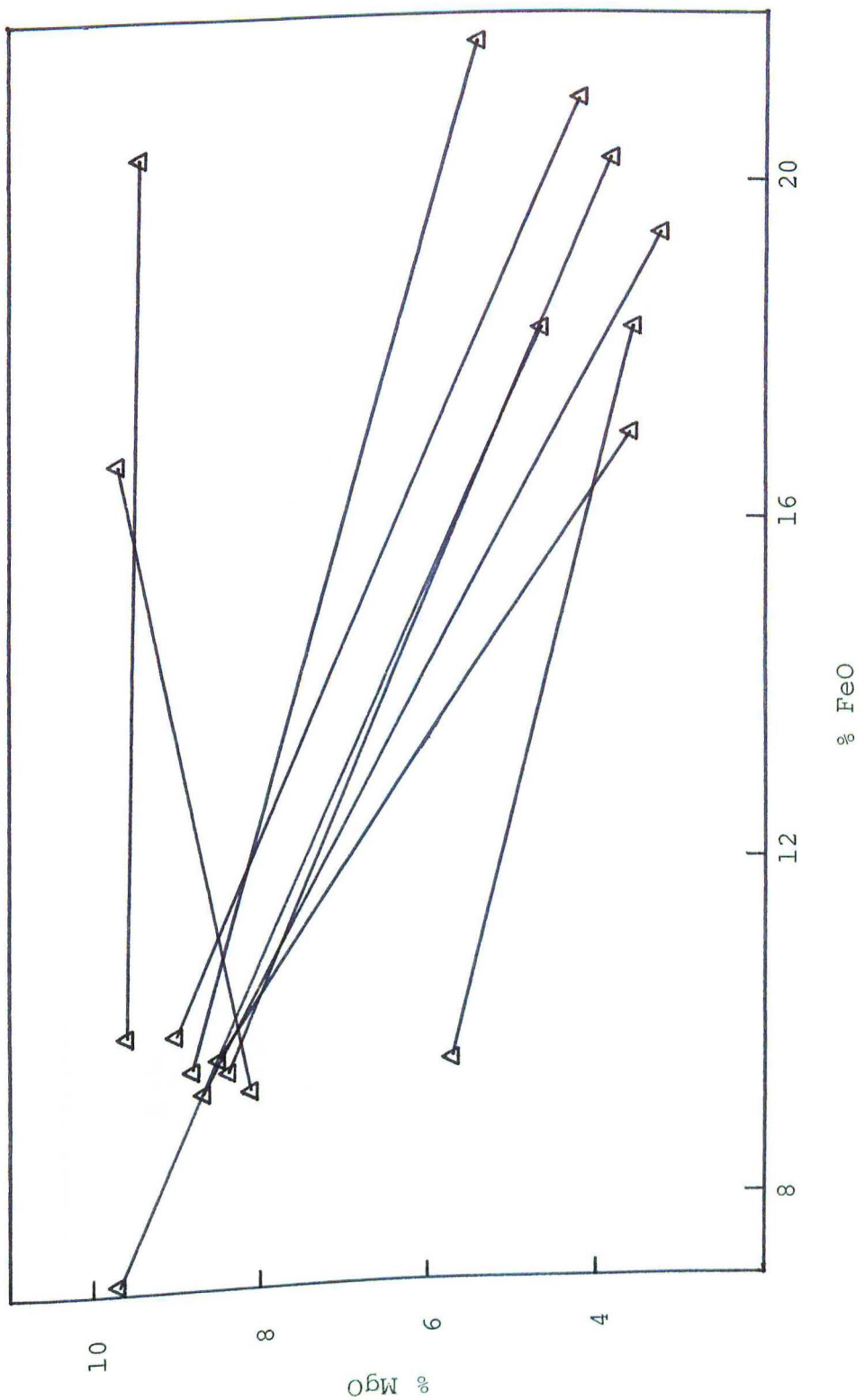
Figure 6	% SiO_2	vs.	% FeO
Figure 7	% Al_2O_3	vs.	% FeO
Figure 8	% MgO	vs.	% FeO
Figure 9	% CaO	vs.	% FeO
Figure 10	% Na_2O	vs.	% FeO
Figure 11	% K_2O	vs.	% FeO
Figure 12	% TiO_2	vs.	% FeO

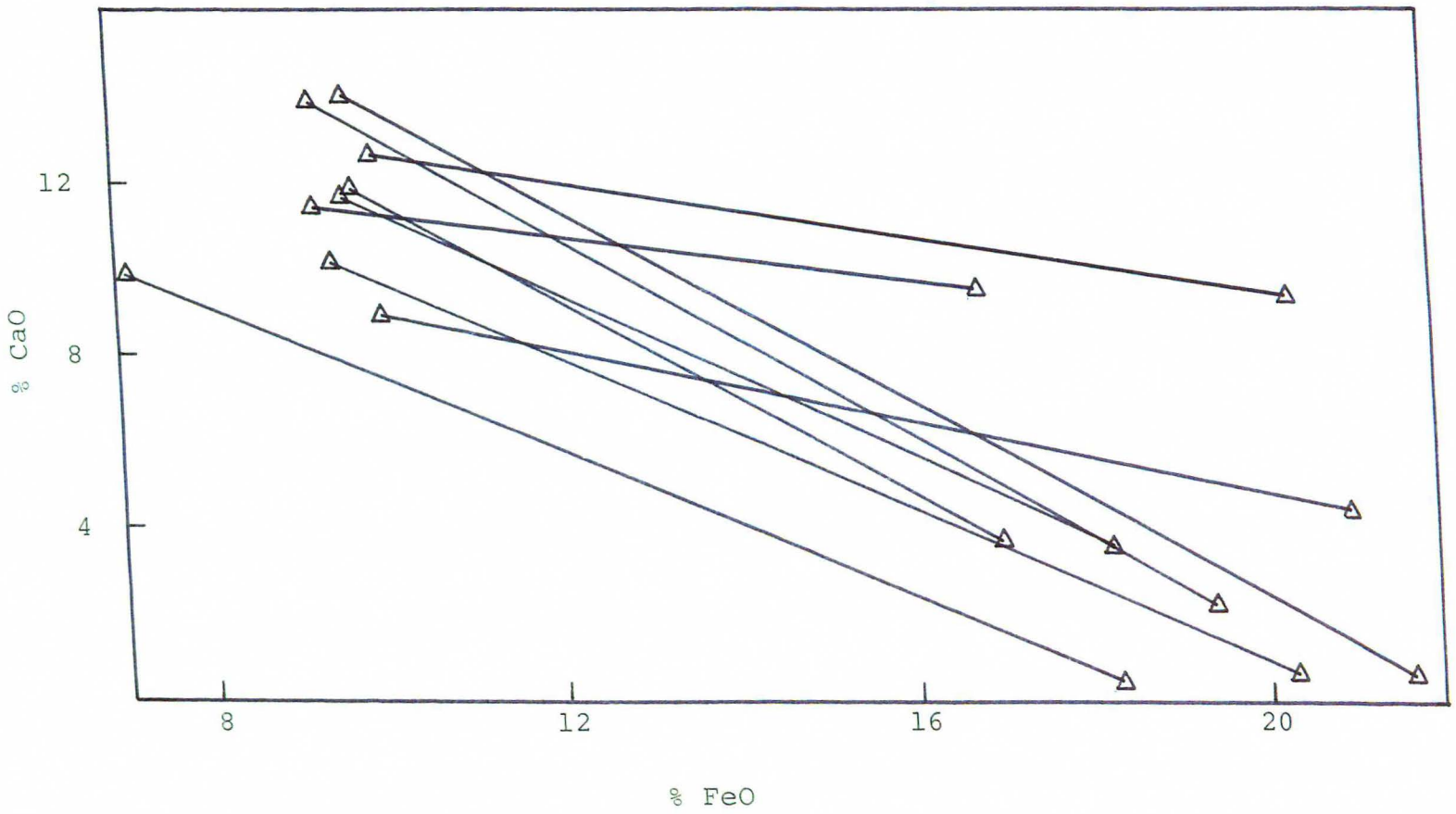
Tie-lines labelled only where similar slopes for samples from the same core are apparent, and other cores differ.

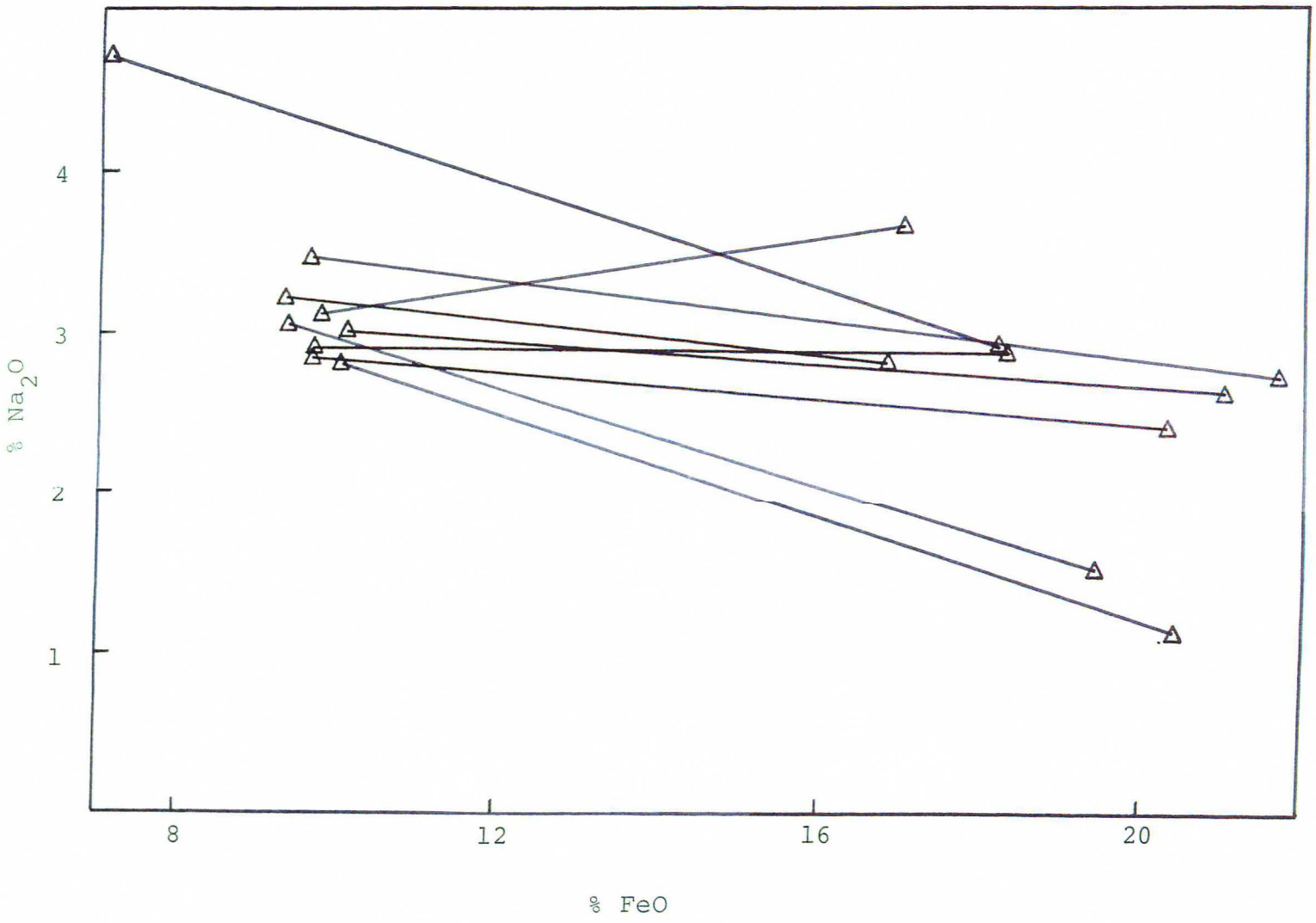
Data tabulated in Appendix B.

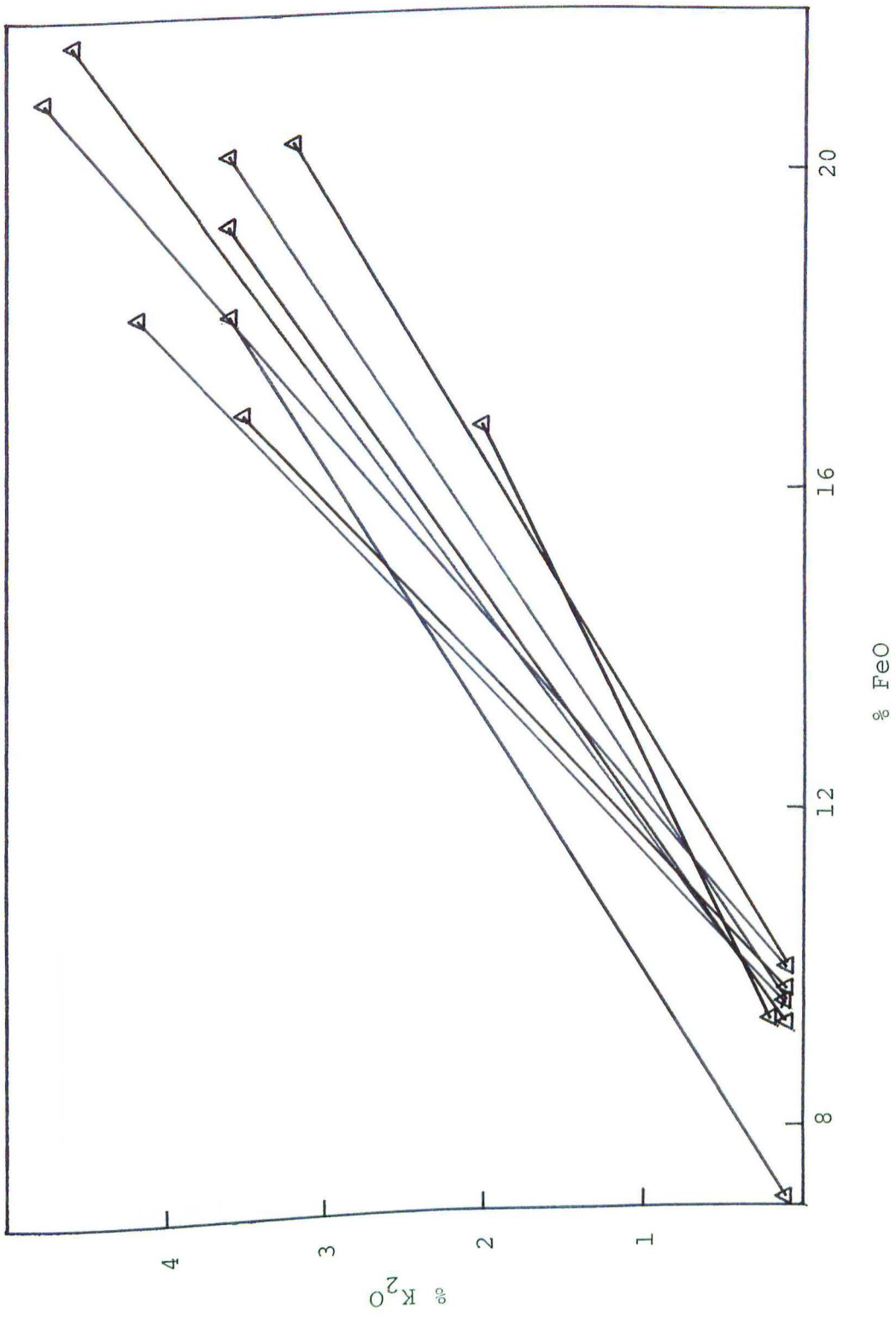

52
50
48
46
% SiO_2
8
12
16
20
% FeO
4-2-3
4-1-4
6-1-1 A
5-2-4
5-2-1
24-1-12
23-1-9
6-1-12
6-1-1 B

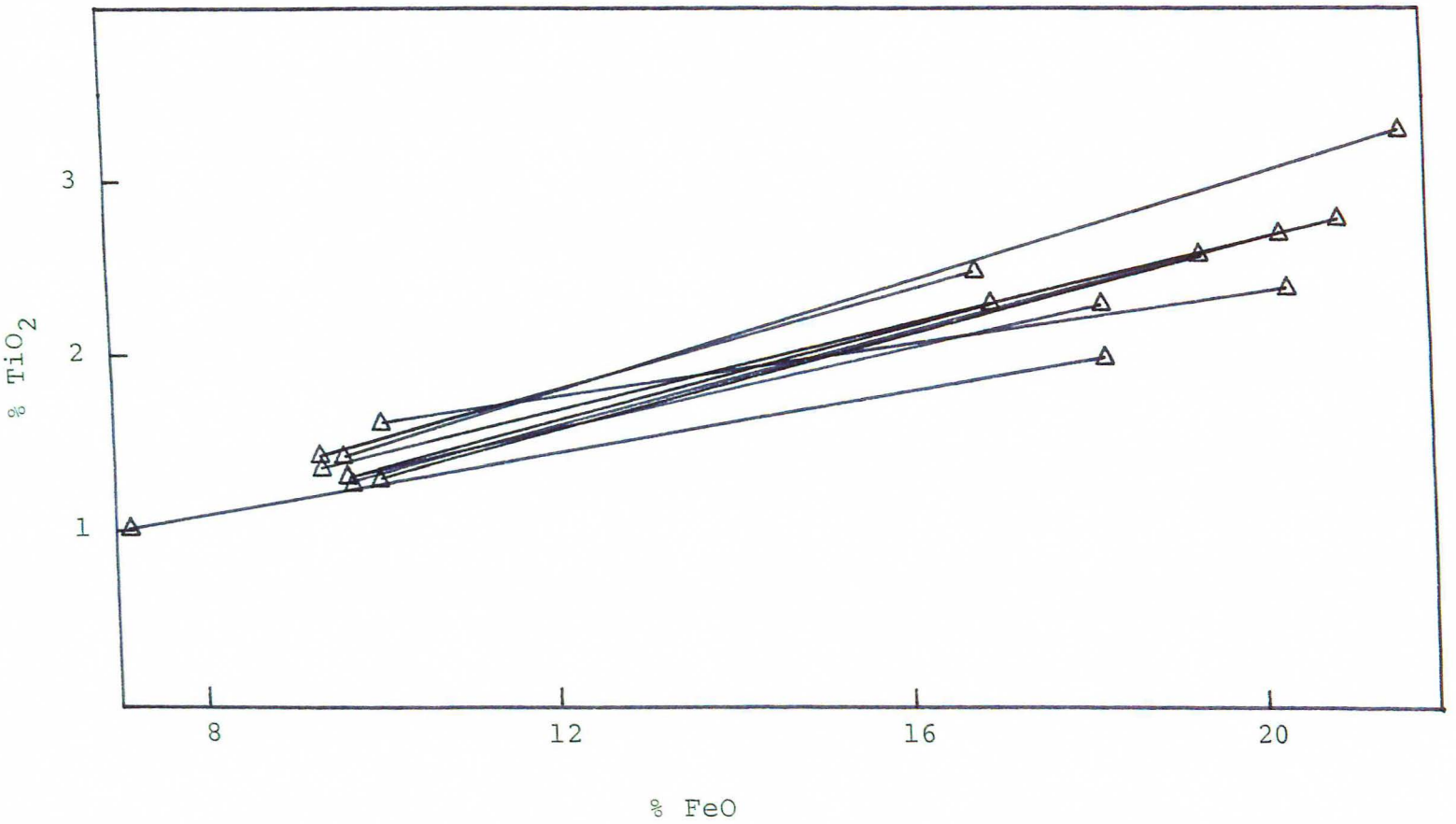

5-2-1
5-2-4
4-1-4
6-1-1 A
6-1-12
4-2-3
6-1-1 B
23-1-9
24-1-12
20
18
16
14
8
12
16
20
% Al_2O_3
% FeO


10
8
6
4
% MgO
8
12
16
20
% FeO


12
8
4
% CaO
8
12
16
20
% FeO


4
3
2
1
% Na_2O
8
12
16
20
% FeO


4
3
2
1
% K_2O
8
12
16
20
% FeO


3
2
1
% TiO_2
8
12
16
20
% FeO

The inhomogeneity of the altered products is evident from the variations in the slopes of the elemental plots. They indicate that the alteration processes operating on this scale are, not unexpectedly, non-uniform, resulting in altered products of variable compositions. Where slopes are very similar, this may indicate that the species is either not greatly mobilized or is easily and uniformly mobilized during alteration.

The plot of % SiO_2 vs % FeO (Figure 6) shows variable changes for Si, by the variations in slope, although samples from the same core show similar slopes. Some Si is retained in the altered glass, forming the palagonite or smectite. Released Si must also be taken up in the formation of phillipsite or other zeolites. With absolute losses on the order of 1-3 weight %, this does not constitute the major loss from the glass. SiO_2 is also lost from altered crystalline samples (Bohlke, 1978; Honnorez et al., 1978).

Varying changes in Al_2O_3 also reflect the non-uniformity of the alteration processes (Figure 7). Al is also retained in the altered glass. Some Al would also be taken up in the formation of the zeolites. However, the ratio of SiO_2:Al_2O_3 in phillipsite of the idealized formula of $(K_2,Na_2,Ca)(Al_2Si_4)O_{12} \cdot 4\text{-}5\ H_2O$ (Fleischer, 1975) is 2.26:1. Thus over twice as much absolute SiO_2 as Al_2O_3 loss may be taken up in phillipsite. Again, the samples from the same core tend to have the same slopes. Overall, there is a

positive slope, but this is very small, and the line not well correlated (low r value).

MgO shows a generally negative slope (Figure 8, Table 7) indicating the release of Mg from the basalt, and that it is not retained in the altered glass. Mg is not greatly retained in either the calcite or zeolite cements, and therefore would be released into solution. Depletions are on the order of 5-6 weight %. Mg appears to be readily mobilized and removed, as major losses were observed in almost all samples.

Calcium is also readily removed, demonstrated by the uniformly negative and steep slopes (Figure 9, Table 7). It is almost uniformly depleted to less than half the original concentrations. Of all the major oxides, it has an average slope closest to 1, and shows the greatest absolute weight % losses, implying that it's loss is most directly related to the decrease in density. Obvious sinks for Ca are the formation of calcite cements and vein fillings. Phillipsite is not a major repository for Ca in these samples. Some cements tentatively identified as calcite contain too much SiO_2 to be entirely calcite (i.e. in 6-1-1 (4-7) B), and may be a Ca-rich zeolite such as chabazite, or an admixture of calcite and zeolite.

The average slope for Na_2O is slightly negative (Figure 10, Table 7). Absolute changes are approximately 1%, but constitute loss of as much as half the original Na_2O. This is in contrast to Bohlke's (1978) results for crystalline

samples from these cores, showing Na_2O to be passively accumulated in crystalline samples,because it is a component of primary, unaltered igneous minerals. In the structure of the glass, where Na is not bound in the same way into the structure, it is apparently more easily released.

The least squares fit of K_2O and FeO shows as high an r value as does that for TiO_2 (Figure 11, Table 7). This might imply that K_2O is also passively accumulated, but its increase to 3-4 times the original content makes this unlikely. The K contained in the authigenic phillipsite cannot be derived from the glass, so both the altered glass and authigenic zeolites are concentrating K from seawater, in the case of the glass proportionate with the loss of other species.

Titanium is strongly colinear with Fe (Figure 12, Table 7). If they are both residual, and therefore passively accumulated, this is to be expected. Ti is not concentrated in either the calcite cements or authigenic zeolites. Its immobility (as discussed earlier), similar to that of Fe, should make it also useful as a normalizing factor.

Hay and Iijima (1968) reported that for the subaerial alteration of volcanic tuffs, the density of the palagonite formed is up to 40% less than that of the fresh glass. In calculated % changes (Appendix B), at a 40% density reduction, elements passively accumulated should show a change of +67%. However, the % changes observed for FeO and TiO_2 are generally on the order of 100% or more, indicating at least a 50% re-

duction in density. Ratios of the oxide compositions to the FeO content are indicative of the net change independent of density changes, and are shown in Table 9. Plots are not included here because the lines lie too close together for clarity. The slope of the tie-lines if these were plotted as were the oxide vs. FeO diagrams are also included in Table 9. Si, Al, Mg, Ca and Na now uniformly decrease. Ti, as should be if it is immobile with respect to Fe, shows virtually no slope. K uniformly increases.

Honnorez (1978) found that a total rock chemical analysis (including fresh glass, altered glass, and authigenic minerals) showed that Si, Al, Fe and Ti are retained in the bulk rock, while K and Na were enriched. He concluded that these last two elements were extracted from seawater which initially had free access between the granules. The loss of Si and Al then, from the altered glass, is not followed by transport out of the basalt column, but by reprecipitation in the form of authigenic minerals. The K and Na depleted in the altered glass relative to the fresh glass, is also retained in the pile, along with additional quantities scavenged from seawater. The removal mechanism for the major part of river-borne Mg from the oceans has not been identified (Holland, 1978). The additional Mg contributed to the oceans by the alteration of crystalline and glassy basalts (Bohlke, 1978; Honnorez, 1978) contributes further to the load of Mg, rather than contributing to its removal.

Table 9

Major oxide / FeO ratios

	4-1-4			4-2-3			5-2-1		
	FG	AG	slope	FG	AG	slope	FG	AG	slope
SiO_2	7.01	2.76	-.38	5.22	2.79	-.28	5.32	2.48	-.28
Al_2O_3	2.48	.97	-.13	1.69	.93	-.09	1.66	1.07	-.06
FeO	1	1		1	1		1	1	
MgO	1.37	.25	-.10	.59	.19	-.05	.94	.17	-.08
CaO	1.39	.02	-.12	1.21	.04	-.13	1.39	.04	-.13
Na_2O	.66	.16	-.04	.30	.15	-.02	.33	.08	-.02
K_2O	.01	.20	+.02	.01	.23	+.03	.01	.19	+.02
TiO_2	.14	.11	.00	.13	.13	.00	.15	.13	.00

Ratios as % oxide/% FeO

Slope as change in oxide species/change in % FeO = $(AG-FG)/(FeO_{AG}-FeO_{FG})$

Table 9 (cont.)

	5-2-4			6-1-1 A			6-1-1 B		
	FG	AG	slope	FG	AG	slope	FG	AG	slope
SiO_2	5.17	2.86	-.31	5.43	2.41	-.28	4.68	2.26	-.23
Al_2O_3	1.69	1.17	-.07	1.67	.88	-.07	1.67	.81	-.08
FeO	1	1		1	1		1	1	
MgO	.87	.21	-.09	.88	.19	-.06	.96	.46	-.05
CaO	1.22	.15	-.15	1.06	.03	-.10	1.22	.03	-.11
Na_2O	.32	.13	-.03	.29	.12	-.02	.28	.06	-.02
K_2O	.01	.20	+.03	.01	.18	+.02	.01	.15	+.01
TiO_2	.13	.14	.00	.13	.13	.00	.16	.12	.00

Table 9 (cont.)

	6-1-12			23-1-9			24-1-12		
	FG	AG	slope	FG	AG	slope	FG	AG	slope
SiO_2	4.83	2.22	-.24	5.30	2.80	-.34	4.88	2.23	-.22
Al_2O_3	1.61	.85	-.07	1.83	.93	-.12	1.74	.62	-.09
FeO	1	1		1	1		1	1	
MgO	.89	.20	-.06	.87	.58	-.04	.92	.25	-.06
CaO	1.15	.02	-.10	1.22	.22	-.13	1.35	.03	-.11
Na_2O	.29	.13	-.01	.34	.17	-.02	.35	.12	-.02
K_2O	.01	.23	+.02	.02	.12	+.01	.02	.21	+.02
TiO_2	.13	.13	.00	.15	.15	.00	.15	.15	.00

The problem in considering the changes occurring during the alteration of the glass based on microprobe analyses is that of whether the analyses (before or after normalizing to 100%) are of equal volumes or of equal weights. Assuming that Fe and Ti are immobile, and that their apparent changes are on the order of over 100%, the data normalized to 100% must be the analysis of equal weights of material. The altered glass however, similar to the open structured material suggested by the isovolumetric changes of Hay and Iijima (1968), has lost major constituents without the total collapse of the structure, and without mobilization of Fe and Ti. The mechanism of the ZAF corrections employed on this EMP system however, involves an iterative procedure predicated on the assumption that all major components are being analyzed. The procedure continues until changes between iterations are less than some predetermined value. Four iterations were typically indicated during these studies. Thus the analyses are on a weight % basis.

However, one gram of fresh glass does not weather to one gram of altered glass. Hay and Iijima's (1968) figures indicate only .6 g would remain. The % changes for FeO and TiO_2 in this study would indicate a somewhat greater density change. The average of 22 such values for FeO is 108 (s.d.= 28), and for TiO_2 is 100 (s.d.=32). The 108% change in FeO is consistent with a density decrease of 52%. Thus from one gram of fresh glass, only .48 g would remain. Table 10

Table 10

Calculation of major elemental changes during alteration

Key

Column 1: Fresh glass composition normalized to 100% (FG)

Column 2: Altered glass composition normalized to 100% (AG)
x FeO_{FG}/FeO_{AG}
representing composition at constant FeO content

Column 3: Column 2 - Column 1 = (AG-FG) = change in g/100 g

Column 4: % change = ((AG-FG)/FG) x 100%

Column 5: Change in grams / 1000 cm^3 glass =
(AG-FG) g/100 g x 28.0 g/10 cm^3 *

Column 6: Change in grams / 1000 cm^3 basalt column =
Column 5 x .25 g glass/g basalt x .25 g glass altered/g glass

*Density of fresh glass from Hay and Iijima (1968)

Table 10 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000cm^3 glass	Δ g/1000cm^3 column
4-1-4						
SiO_2	49.76	19.61	-30.15	- 61	-844	-53
Al_2O_3	17.61	6.86	-10.75	- 61	-301	-19
FeO	7.10	7.10	0	0	0	0
MgO	9.72	1.78	- 7.94	- 82	-222	-14
CaO	9.87	.15	- 9.72	- 98	-272	-17
Na_2O	4.72	1.13	- 3.59	- 76	-100	- 6
K_2O	.10	1.39	+ 1.29	+1290	+ 36	+ 2
TiO_2	1.01	.79	- .22	- 22	- 6	- 0.4
FeO_{FG}/FeO_{AG} = .39						
4-2-3						
SiO_2	49.97	26.77	-23.20	- 46	-650	-41
Al_2O_3	16.16	8.90	- 7.26	- 45	-203	-13
FeO	9.58	9.58	0	0	0	0
MgO	5.70	1.86	- 3.84	- 67	-108	- 7
CaO	11.59	.39	-11.20	- 97	-314	-20
Na_2O	2.90	1.47	- 1.43	- 49	- 40	- 3
K_2O	.10	2.20	+ 2.10	+2100	+ 59	+ 4
TiO_2	1.26	1.21	- .05	- 4	- 1	- 0.1
FeO_{FG}/FeO_{AG} = .52						

Table 10 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000cm^3 glass	Δ g/1000cm^3 column
5-2-1						
SiO_2	49.31	23.01	-26.30	- 53	-736	-46
Al_2O_3	15.40	9.96	- 5.44	- 35	-152	-10
FeO	9.27	9.27	0	0	0	0
MgO	8.73	1.55	- 7.18	- 82	-201	-13
CaO	12.85	.36	-12.49	- 97	-350	-22
Na_2O	3.04	.70	- 2.34	- 77	- 66	- 4
K_2O	.12	1.72	+ 1.60	+1333	+ 45	+ 3
TiO_2	1.35	1.23	- .12	- 9	- 4	- 0.2
FeO_{FG}/FeO_{AG} = .48						
5-2-4						
SiO_2	50.35	27.83	-22.52	- 45	-631	-39
Al_2O_3	16.49	11.41	- 5.08	- 31	-142	- 9
FeO	9.74	9.74	0	0	0	0
MgO	8.47	2.08	- 6.39	- 75	-179	-11
CaO	11.89	1.42	-10.47	- 88	-293	-18
Na_2O	3.08	1.24	- 1.84	- 60	- 52	- 3
K_2O	.11	1.99	+ 1.88	+1709	+ 53	+ 3
TiO_2	1.26	1.32	+ .06	+ 5	+ 2	+ 0.1
FeO_{FG}/FeO_{AG} = .57						

Table 10 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000 cm^3 glass	Δ g/1000 cm^3 column
6-1-1 A						
SiO_2	51.87	22.98	-28.89	- 56	-809	-51
Al_2O_3	15.99	8.37	- 7.62	- 48	-214	-13
FeO	9.55	9.55	0	0	0	0
MgO	8.36	1.79	- 6.57	- 79	-184	-12
CaO	10.16	.32	- 9.84	- 97	-276	-17
Na_2O	2.76	1.12	- 1.64	- 60	- 46	- 3
K_2O	.10	1.67	+ 1.57	+1570	+ 44	+ 3
TiO_2	1.24	1.25	+ .01	+ 1	+ 28	+ 2
FeO_{FG}/FeO_{AG} = .47						
6-1-1 B						
SiO_2	46.92	22.62	-24.30	- 52	-680	-43
Al_2O_3	16.79	8.14	- 8.65	- 52	-242	-15
FeO	10.03	10.03	0	0	0	0
MgO	9.59	4.64	- 4.95	- 52	-139	- 9
CaO	12.26	.33	-11.93	- 97	-334	-21
Na_2O	2.82	.56	- 2.26	- 80	- 63	- 4
K_2O	.10	1.55	+ 1.45	+1450	+ 41	+ 3
TiO_2	1.56	1.20	- .36	- 23	- 10	- 0.6
FeO_{FG}/FeO_{AG} = .49						

Table 10 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000cm^{3}glass	Δ g/1000cm^{3}column
6-1-12						
SiO_2	48.64	22.34	-26.30	- 54	-736	-46
Al_2O_3	16.23	8.53	- 7.70	- 47	-216	-14
FeO	10.08	10.08	0	0	0	0
MgO	9.01	1.99	- 7.02	- 78	-197	-12
CaO	11.64	.23	-11.41	- 98	-319	-20
Na_2O	2.97	1.27	- 1.70	- 57	- 48	- 3
K_2O	.12	2.29	+ 2.17	+1808	+ 61	+ 4
TiO_2	1.26	1.33	+ .07	+ 6	+ 2	+ 0.1
FeO_{FG}/FeO_{AG} = .48						
23-1-9						
SiO_2	49.51	26.11	-23.40	- 47	-655	-41
Al_2O_3	17.07	8.67	- 8.40	- 49	-235	-15
FeO	9.34	9.34	0	0	0	0
MgO	8.12	5.42	- 2.70	- 33	- 76	- 5
CaO	11.41	2.05	- 9.36	- 82	-262	-16
Na_2O	3.22	1.55	- 1.67	- 52	- 47	- 3
K_2O	.18	1.10	+ .92	+ 511	+ 26	+ 2
TiO_2	1.38	1.37	- .01	- 1	- 0.3	0
FeO_{FG}/FeO_{AG} = .56						

Table 10 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000cm^3 glass	Δ g/1000cm^3 column
24-1-12						
SiO_2	47.00	21.43	-25.57	- 54	-716	-45
Al_2O_3	16.78	5.97	-10.81	- 64	-303	-19
FeO	9.63	9.63	0	0	0	0
MgO	8.82	2.41	- 6.41	- 73	-180	-11
CaO	13.01	.27	-12.74	- 98	-357	-22
Na_2O	3.37	1.19	- 2.18	- 65	- 61	- 4
K_2O	.17	2.03	+ 1.86	+1094	+ 52	+ 3
TiO_2	1.42	1.48	+ .06	+ 4	+ 2	+ 0.1

FeO_{FG}/FeO_{AG} = .44

Table 10 (cont.)

Average values

	AG-FG	s.d.	Δ %	s.d.	Δ g/ 1000 cm^3 glass	s.d.	Δ g/ 1000 cm^3 column	s.d.
SiO_2	-25.63	2.46	- 52	5	-717	69	-45	4
Al_2O_3	- 7.97	1.88	- 48	10	-223	53	-14	3
FeO	0		0		0		0	
MgO	- 5.89	1.61	- 69	15	-165	45	-10	3
CaO	-11.02	1.17	- 95	5	-309	33	-19	2
Na_2O	- 2.07	.61	- 64	11	- 58	17	- 4	1
K_2O	+ 1.65	.38	+1429	432	+ 46	11	+ 3	1
TiO_2	- .06	.14	- 5	10	+ 1	10	+ 0.1	0.6

SiO_2	-179 *
Al_2O_3	- 8
FeO	+ 1
MgO	-106
CaO	- 3
Na_2O	+ 0.3
K_2O	+ 0.2
TiO_2	+ 0.3

* from Bohlke (1978), Δ g/ 1000 cm^3 basalt

repeats the fresh glass data from Table 8, along with the altered glass values multiplied by a factor (FeO in fresh glass/FeO in altered glass) to yield equal values of FeO. This now represents the weight in g/100g remaining in the altered glass. Table 10 also shows the weight of each oxide lost, and the percent this represents of the original glass composition. A computation is also shown of 'change/1000cm^3 of glass' based on the difference between the 100g of fresh glass and altered glass x 2.8 g/cm^3 x 10 to yield $g/1000cm^3$. This then represents the material lost when $1000cm^3$ or 2.78 kg of glass is totally altered to smectite. Obviously, the basalt does not exist as 100% glass, and the glass is not totally altered. Taking an estimate of 25% glass being 25% altered (Dmitriev, Heirtzler et al., 1978), gives an estimate of the change as a result of glass alteration / $1000cm^3$ of basalt column. Averages of these values are also shown in Table 10, along with a similar calculation for the crystalline basalts from these cores (Bohlke, 1978).

Comparing the figure for total glass alteration, the glass can be seen to show greater changes than the basalt. This is in general agreement with the work of others (Lipman, 1965; Thompson, 1973), and is not unexpected, since the glass is the less stable phase. The estimate of the materials released based on 25% glass present, and it being 25% altered, shows greater effects for the glass for Al, Ca, Na and K than for the crystalline basalts. The only species showing another

direction of change is Na. Bohlke (1978) considers Na to be passively accumulated, and this is reasonable in light of its presence as part of unaltered primary igneous minerals. However, in the glass, where the cations are located randomly in a less orderly silicate network (Bartenev, 1970), the disruption of that net allows the release of Na. It must be noted that the figures for the alteration of glass to smectite do not include authigenic minerals formed, as Bohlke's analyses of bulk altered basalts must.

Table 11 is reproduced from Furnes (1978) for comparison. Furnes regarded Fe to have been lost during alteration, while Hay and Iijima (1968), Hoppe (1941) and Jakobsson (1972) found small changes or calculated on the basis of no Fe change. Honnorez (1972) found an increase in Fe. Losses of K are reported (Hay and Iijima, 1968; Jakobsson, 1972; Furnes, 1978) when sideromelane is altered in a non-marine environment.

According to Honnorez (1978), however, the alteration of glass results in the deposition of authigenic minerals that entirely absorb the released products (except for Mg), and also remove Na and K from seawater. In the formation of phillipsite, the limiting elements must be Al and Si, since they are derived from the basalt while the alkali metals may be scavenged from seawater (Honnorez, 1978). The ratio of average lost SiO_2 to Al_2O_3 is 3.22. This is greater than the theoretical value of 2.25 calculated earlier. The average of phillipsites analyzed is 2.53 (n=8, s.d.=.15). This leaves

Table 11

Comparison of chemical changes (%) from Furnes (1978)

	Furnes (1978)	Hay and Iijima (1968)	Hoppe (1941)	Jakobsson (1972)	Honnorez (1972)
SiO_2	- 40	- 28	- 53	- 75	- 11
Al_2O_3	- 24	- 54	- 59	- 84	- 24
FeO	- 31	- 1	0	0	+ 42
MgO	- 51	- 47	- 58	- 63	+ 12
CaO	- 66	- 74	- 50	- 89	+ 2
Na_2O	- 47	- 96	- 80	- 99	- 74
K_2O	- 79			- 98	0
TiO_2	- 46	- 16	0	- 18	+ 49
MnO	- 32		0		

some Si unaccounted for, that is not precipitated as phillipsite. The high Ca cements which still contain some Si, presumably an admixture of calcite and zeolite, show even lower SiO_2:Al_2O_3 ratios. The amount of phillipsite precipitated is therefore controlled by the amount of Al released, with some Si presumably remaining in solution.

The major sink for Ca is calcite or Ca-rich cements. Mg is not retained in the altered glass, nor to any great extent by the other authigenic minerals, and must therefore be released into solution. Both these species are lost from the basalt column (Honnorez, 1978) although some Ca is retained in the cements. The ratio of weight % CaO/MgO lost is 1.87. The Ca-rich cement have ratios of approximately 20. The loss of one gram of CaO would require the precipitation of 1.78 g of $CaCO_3$. Calcium rich cements do not seem to be as ubiquitous as would be required to contain all the lost Ca, in fact being entirely absent in many sample sections.

The ratio of average lost Al_2O_3/NaO in g/100g of fresh glass is 3.85. In the phillipsites analyzed it is 2.84 (s.d.=.88) ranging from 1.28 to 4.62. Not all of the released Na is retained in the phillipsites - some is retained in the high Ca cements. However, the difference in the two ratios for the fresh glasses and the phillipsites indicates an enrichment factor of 1.4 for the Na, slightly less than the factor of 1.8 to 3.3 reported for the total basalt unit by Honnorez (1978) when considering all authigenic phases.

Bloch and Bischoff (1979) examined the effect of the low-temperature alteration of basalt on oceanic mass balances for K. They state that palagonitization plays a minor role in the oceanic budget of K, but regard 'fracture-controlled alteration' that results in the formation of K-rich phases such as smectites and zeolites as having a major role. This view separates the total effects of the alteration of glasses into two processes - palagonitization and authigenic mineral formation - although these two are the end products of the same process.

Trace Elements (Milliprobe Analyses)

In XRF analyses, the ideal situation is when the matrices of the samples are the same as that of the standards. This is particularly the goal in heavy-absorber fusion preparations (Jenkins and deVries, 1978) but such preparations do not allow the desired separation of fresh and altered material. The initial intent in determining Fe along with the trace metals was to correct for its absorption effect on Zn, Cu and Ni, and its enhancement of Cr. However, when this correction was attempted using the XRF-4 program (Marr, 1976a; Marr, 1976b) the effect of Fe was calculated as an enhancement of Zn, Cu and Ni - not a reasonable result, and did not offer significant improvement for Cr.

The fit of a standard curve of course does not have anything to do with the compositions of the samples, only that of the standards. Estimates of the total mass absorption of the standards at 1.6 Å (excluding oxygen) yielded values of 77-67, decreasing with FeO content. Estimates on the samples, based on microprobe analyses not normalized to 100% (hoping to partially include the effects of increased porosity) yielded values of 67-68 for fresh glasses, and 67-69 for altered glasses. In fact, if the analyses are considered to be of equal volumes, the decreased density and increased porosity of

the smectite should result in overestimation of trace metal levels in the altered glass, rather than underestimation, in spite of the higher Fe content. If the increased Fe content measured is a result of decreased density, then the trace metals, if immobile, should be similarly affected. As shall be shown, however, they are observed to be almost universally lost from the fresh glass - smectite system.

The milliprobe data is tabulated in Appendix C, along with % change calculations on the unnormalized data. In order to smooth out local effects, as with the microprobe data, averages of analyses have been reported. Due to the restrictions imposed on the choice of analysis sites by the sample siting procedure, fewer analyses are presented. Where more than one fresh glass - altered glass pair has been analyzed in a single sample, they have been retained separately here where they may not have been for the EMP data. Plots similar to those prepared for the major elements are shown in Figures 13-17. The trends are generally less clear than for the major elements.

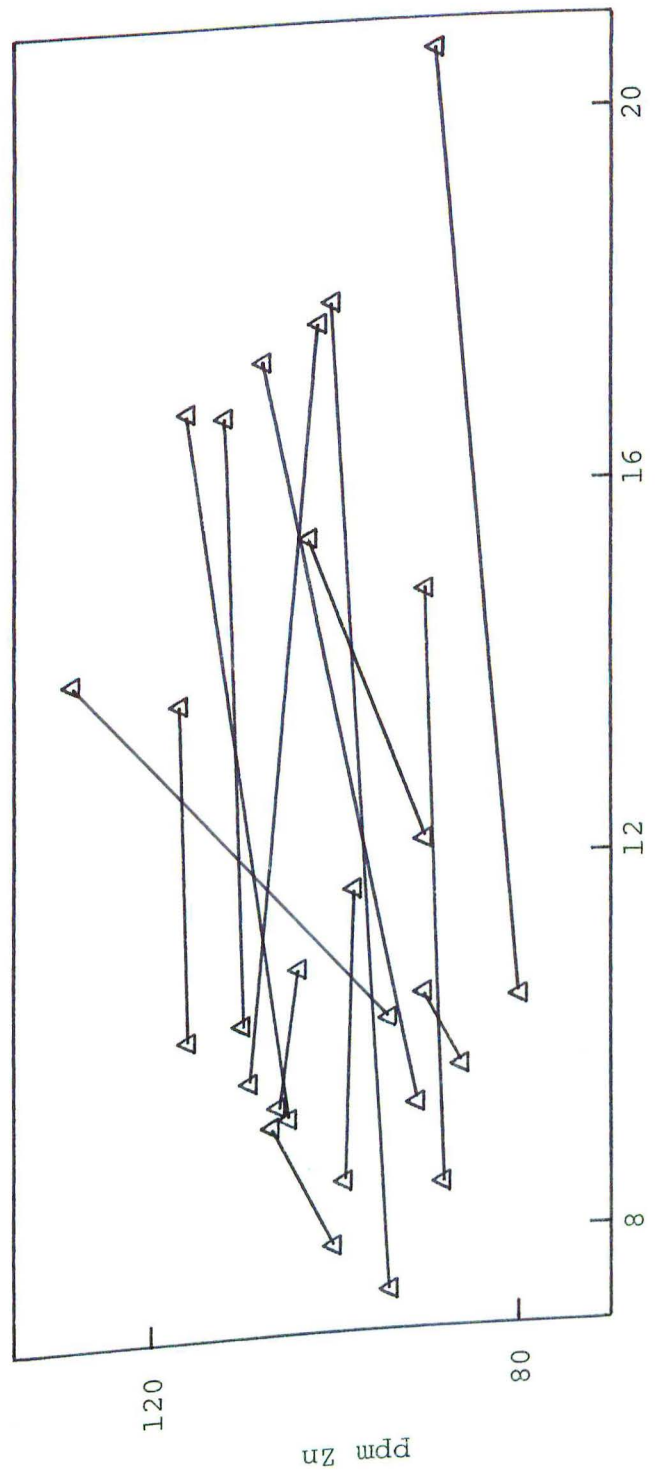
It is obvious when comparing these plots to those for the major elements, that there is not the clustering of the extreme ends of the tie-lines relative to the FeO axis that there was for the major elements. This is most likely because of the inclusion of some fresh or altered glass included in the analysis of the other, either due to positional error, or the intrusion of the undesired material below the

Plots of XMP FG - AG Pair Data

Figure 13	ppm Zn	vs.	% FeO
Figure 14	ppm Cu	vs.	% FeO
Figure 15	ppm Ni	vs.	% FeO
Figure 16	% MnO	vs.	% FeO
Figure 17	ppm Cr	vs.	% FeO

Tie lines labelled only where similar slopes for samples from the same core are apparent, and other cores differ.

Data tabulated in Appendix C.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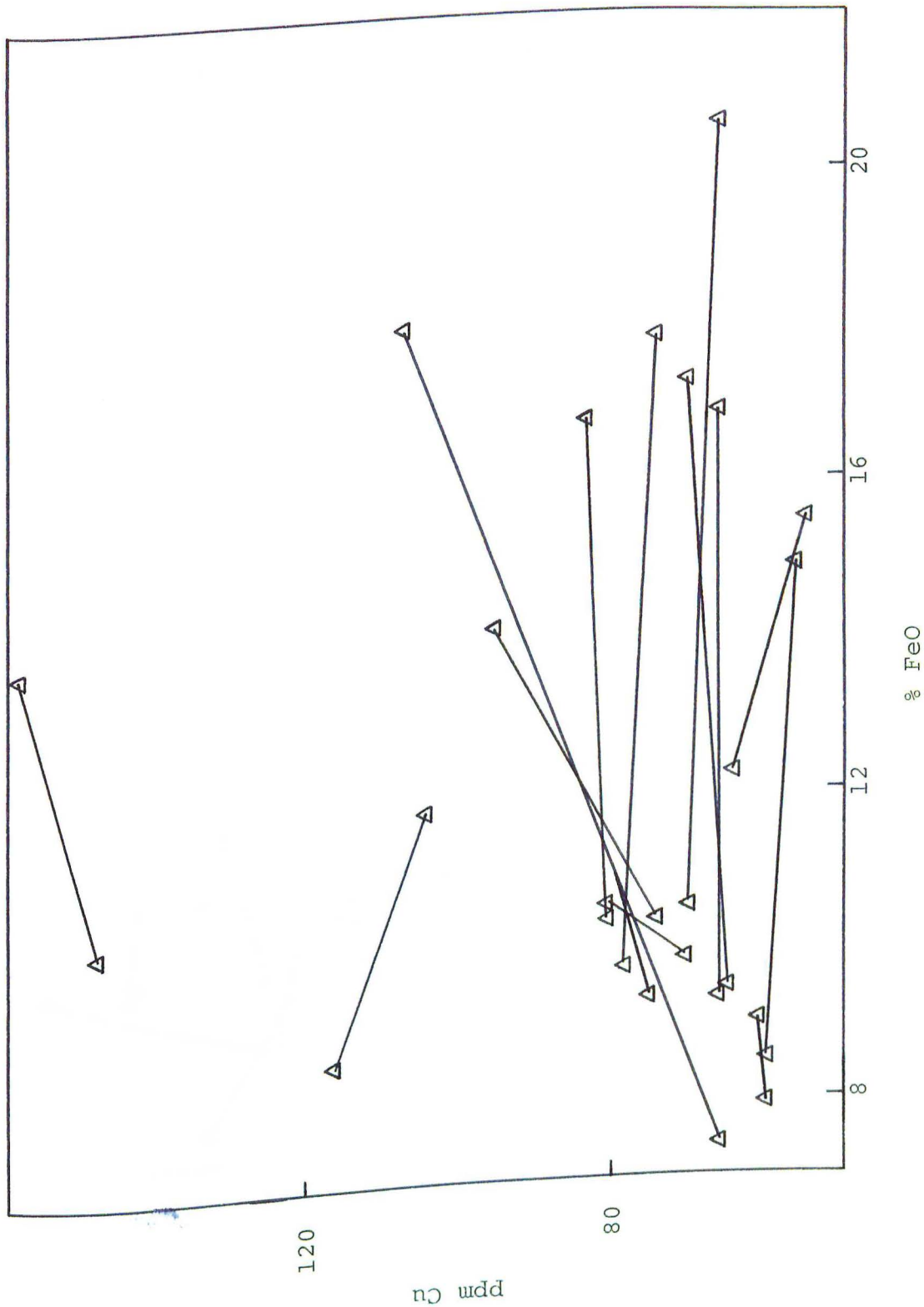
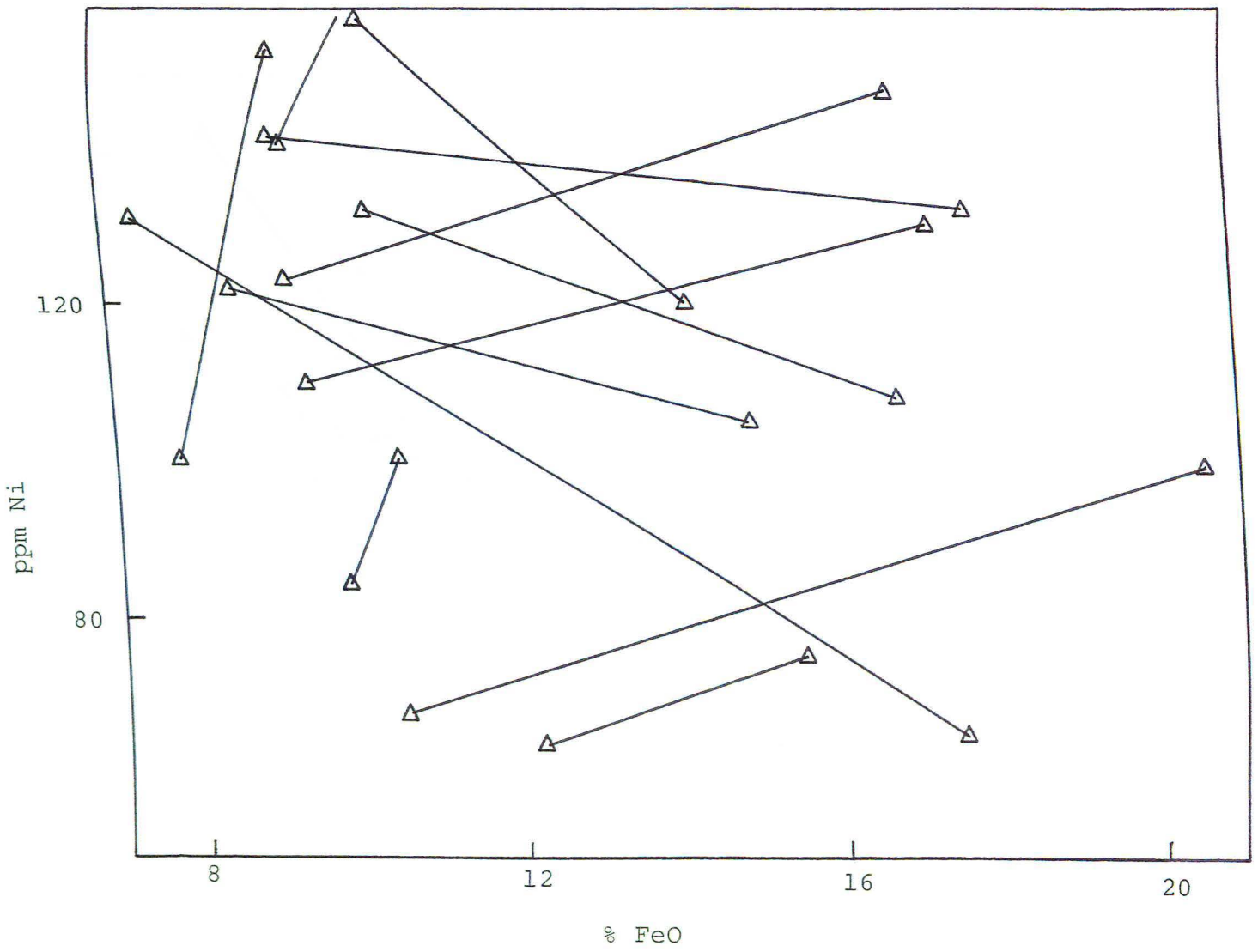
120
80
8
12
16
20
% FeO


ppm Cu
120
80
8
12
16
20
% FeO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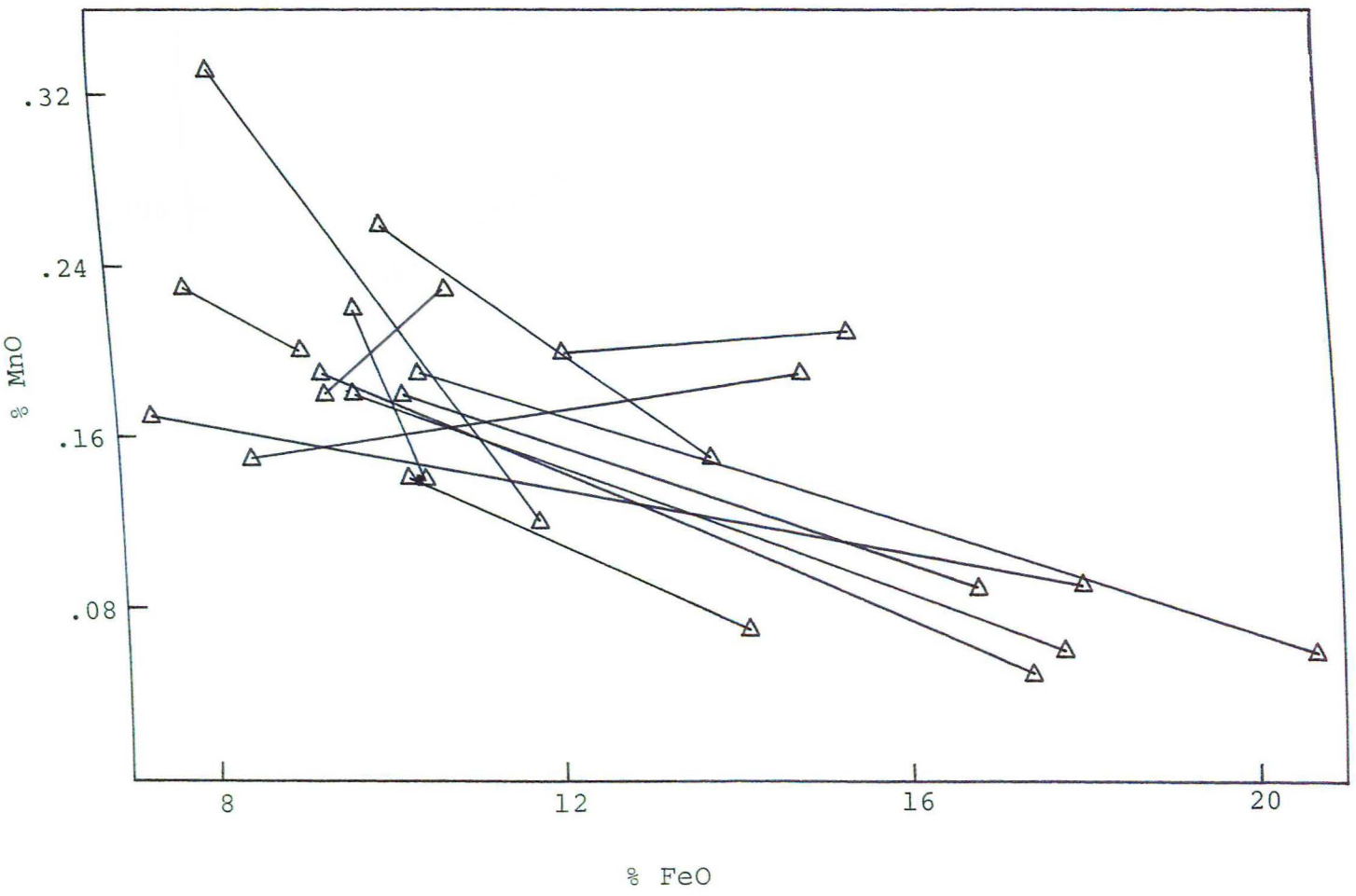
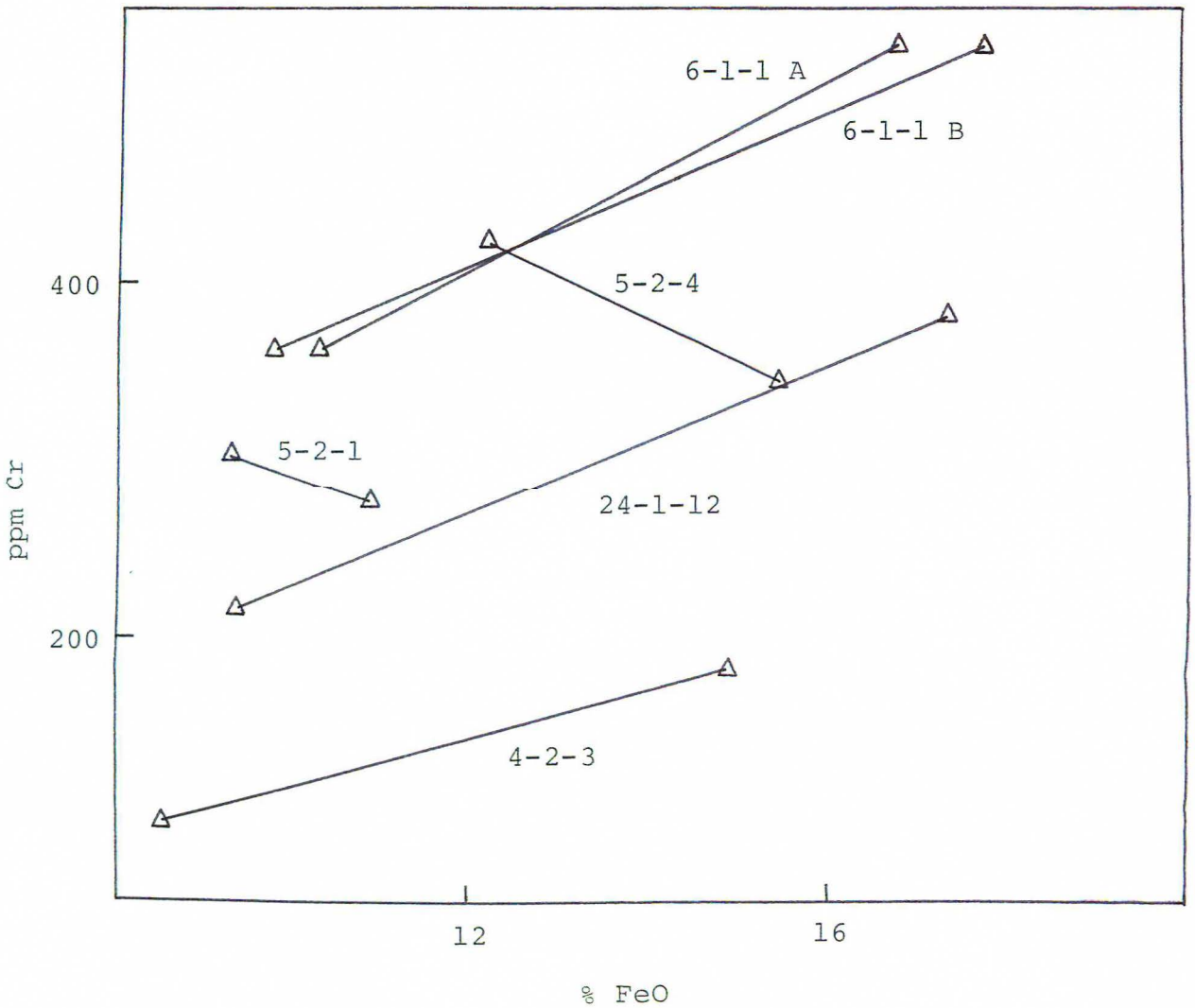
80
ppm Ni
8
12
16
20
% FeO


.32
.24
.16
.08
% MnO
8
12
16
20
% FeO


6-1-1 A
6-1-1 B
5-2-4
5-2-1
24-1-12
4-2-3
400
200
ppm Cr
12
16
% FeO

surface, where it could not be seen but was within the volume being analyzed. Normalization of EMP analyses to 100% would also have the effect of moving the endpoints, with respect to Fe, closer together. The XMP analyses have not been normalized in that fashion.

The Zn tie-lines (Figure 13) show either an increase or no change in the Zn content, relative to changes in Fe. When normalized to constant Fe, however, they universally show a loss of Fe (to be discussed later). Even for samples where more than one pair has been plotted, the tie-lines do not show the same slope.

Tie-lines for Cu also show no definite trend, again with no agreement for pairs from the same sample (Figure 14). Ni shows even greater scatter (Figure 15). MnO shows a general decrease (Figure 16), and Cr shows a general increase, with agreement in the direction of change for pairs from the same core (Figure 17).

Calculated ratios of concentration of metal/ % FeO and the slopes of these tie-lines if plotted against FeO are shown in Table 12. Unlike the similar figures for the major elements, this calculation does not result in uniform slopes. This suggests that the processes involved are highly non-uniform, and vary greatly with local alteration conditions. Thompson (1973) examined trace metal trends in the alteration of three different pillows, representing varying degrees of alteration, and reported conflicting trends for

Table 12

Trace metal/FeO ratios

	4-1-4			4-2-3			5-2-1 A		
	FG	AG	slope	FG	AG	slope	FG	AG	slope
Zn	12.79	5.53	- .68	10.34	5.97	- .68	11.39	8.50	- .81
Cu	8.98	5.92	- .29	7.05	3.76	- .51	14.44	11.41	- .85
Ni	17.82	3.60	-1.33	14.34	7.05	-1.14			
FeO	1	1		1	1		1	1	
MnO	.02	.02	.00	.02	.01	.00	.03	.01	- .01
Cr				11.16	12.15	+ .15			

Ratios as ppm metal/% FeO, except for MnO as % MnO/% FeO

Slope as change in metal species/change in % FeO = (AG-FG)/ (FeO_{AG}-FeO_{FG})

Table 12 (cont.)

	5-2-1 B			5-2-1 C			5-2-4 A		
	FG	AG	slope	FG	AG	slope	FG	AG	slope
Zn	11.35	9.57	-1.16	8.82	8.59	- .32	7.39	6.66	- .22
Cu	8.03	7.18	- .56	7.18	7.63	+ .62	5.25	3.56	- .52
Ni	14.88	16.74	+1.22	8.62	9.54	+1.26	5.25	4.85	- .12
FeO	1	1		1	1		1	1	
MnO	.02	.02	.00	.02	.01	- .01	.02	.01	.00
Cr	32.44	25.39	-4.61				34.65	22.38	-3.74

	5-2-4 B			6-1-1 A			6-1-1 B		
	FG	AG	slope	FG	AG	slope	FG	AG	slope
Zn	11.35	6.86	- .59	11.21	5.72	- .68	10.70	6.67	- .62
Cu	7.14	3.90	- .42	8.02	4.15	- .48	7.68	4.94	- .42
Ni	13.30	8.69	- .60	14.51	7.40	- .88	12.84	6.43	- .98
FeO	1	1		1	1		1	1	
MnO	.02	.01	.00	.02	.00	.00	.02	.01	.00
Cr				37.35	29.73	- .94	35.41	31.69	- .57

Table 12 (cont.)

	6-1-12			8-1-13			23-1-9 A		
	FG	AG	slope	FG	AG	slope	FG	AG	slope
Zn	7.59	4.31	- .32	12.71	11.69	- .80	11.46	8.30	-1.00
Cu	6.64	3.19	- .34	7.50	6.67	- .65	13.43	8.81	-1.46
Ni	6.45	4.79	- .16	12.71	16.61	+3.05			
FeO	1	1		1	1		1	1	
MnO	.02	.00	.00	.03	.02	- .01	.04	.01	-.01
Cr									

	23-1-9 B			24-1-12		
	FG	AG	slope	FG	AG	slope
Zn	9.13	9.14	.00	9.65	6.22	- .43
Cu	7.18	6.73	- .12	6.89	4.03	- .36
Ni	15.15	8.43	-1.76	11.66	7.49	- .53
FeO	1	1		1	1	
MnO	.01	.00	.00	.02	.00	.00
Cr				23.12	22.02	- .14

most trace elements, including Cr and Ni, without considering Fe to be constant.

Table 13 shows trace metal levels recalculated on the basis of constant FeO. Even when some of the Fe content may be derived from the undesired phase, these figures should display a relationship representing the loss or gain of the metal in the alteration of a given weight of glass, to whatever extent it has been altered. Table 13 also includes calculations of the difference between the fresh and altered glasses, the % change, change in grams for the alteration of $1000\,cm^3$ of glass, and for $1000 cm^3$ of basalt column, on the same basis as for the major elements. Averages for each are also shown in the table.

The enormous variability in each species is apparent from the concentration data and in the large standard deviations of the averages. The losses of Zn, Cu, Ni and Cr per $1000 cm^3$ of basalt column are less than 100 mg per element. These metals are not entirely absent from the authigenic phillipsite and calcite formed, but these cements are of an entirely different matrix than the standards, and quantitative determinations cannot be highly accurate. Bernat and Church (1978) studied deep-sea zeolites but did not report data on these metals. Some Zn, Cu, Ni and Cr are retained in the cements and phillipsites, but without an accurate determination of the quantities present in these phases, total flux cannot be calculated.

Table 13

Calculation of trace elemental changes during alteration

Column 1: Fresh glass composition (FG) *

Column 2: Altered glass composition (AG) * x FeO_{FG}/FeO_{AG} representing composition at constant FeO content

Column 3: Column 2 - Column 1 = (AG-FG) = change in g/100 g **

Column 4: % change = ((AG-FG)/FG) x 100%

Column 5: Change in grams / 1000 cm^3 glass = (AG-FG) g/100 g x 28.0 g/10 cm^3 ** ***

Column 6: Change in grams / 1000 cm^3 basalt column = Column 5 x .25 g glass/g basalt x .25 g glass altered/g glass **

*Zn, Cu, Ni and Cr as ppm; FeO and MnO as % oxide

**Values for Zn, Cu, Ni and Cr must be multiplied by 10^{-4} to get grams from ppm

***Density of fresh glass from Hay and Iijima (1968)

Table 13 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000cm^{3}glass	Δ g/1000cm^{3}column
4-1-4						
Zn	94	41	- 53	-56	-1484	- 93
Cu	66	44	- 22	-33	- 616	- 39
Ni	131	26	-105	-80	-2940	-184
FeO	7.35	7.35	0	0	0	0
MnO	.17	.04	- .13	-76	- 3.6	- .23
Cr						
FeO_{FG}/FeO_{AG} = .41						
4-2-3						
Zn	88	51	- 37	-42	-1036	- 65
Cu	60	32	- 28	-47	- 784	- 49
Ni	122	60	- 62	-51	-1736	-108
FeO	8.51	8.51	0	0	0	0
MnO	.15	.11	- .04	-27	- 1.1	- .07
Cr	95	103	+ 8	+ 8.4	+ 224	+ 14
FeO_{FG}/FeO_{AG} = .57						
5-2-1 A						
Zn	116	87	- 29	- 25	- 812	- 51
Cu	147	116	- 31	- 21	- 868	- 54
Ni						
FeO	10.18	10.18	0	0	0	0
MnO	.26	.11	+ .15	+136	+ 4.2	+ .26
Cr						
FeO_{FG}/FeO_{AG} = .74						

Table 13 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000cm^{3}glass	Δ g/1000cm^{3}column
5-2-1 B						
Zn	106	89	- 17	-16	- 476	- 30
Cu	75	67	- 8	-11	- 224	- 14
Ni	139	156	+ 17	+12	+ 476	+ 30
FeO	9.34	9.34	0	0	0	0
MnO	.18	.20	+ .02	+11	+ .56	+ .04
Cr	303	237	- 66	-22	-1848	-116
FeO_{FG}/FeO_{AG} = .86						
5-2-1 C						
Zn	86	84	- 2	- 2.3	- 56	- 3.5
Cu	70	74	+ 4	+ 5.7	+ 112	+ 7.0
Ni	84	93	+ 9	+11	+ 252	+ 16
FeO	9.75	9.75	0	0	0	0
MnO	.22	.14	- .08	-36	- 2.2	- .14
Cr						
FeO_{FG}/FeO_{AG} = .93						
5-2-4 A						
Zn	90	81	- 9	-10	- 252	- 16
Cu	64	43	- 21	-33	- 588	- 37
Ni	64	59	- 5	- 7.8	- 140	- 8.7
FeO	12.18	12.18	0	0	0	0
MnO	.20	.17	- .03	-15	- .84	- .05
Cr	422	273	-149	-35	-4172	-261
FeO_{FG}/FeO_{AG} = .79						

Table 13 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000cm^3 glass	Δ g/1000cm^3 column
5-2-4 B						
Zn	105	63	- 42	-40	-1176	- 74
Cu	66	36	- 30	-45	- 840	- 52
Ni	123	80	- 43	-35	-1204	- 75
FeO	9.25	9.25	0	0	0	0
MnO	.20	.10	- .10	-50	- 2.8	- .18
Cr						
FeO_{FG}/FeO_{AG} = .55						
6-1-1 A						
Zn	109	56	- 53	-49	-1484	- 93
Cu	78	40	- 38	-49	-1064	- 66
Ni	141	72	- 69	-49	-1932	-121
FeO	9.72	9.72	0	0	0	0
MnO	.18	.03	- .15	-83	- 4.2	- .26
Cr	363	289	- 74	-20	-2072	-130
FeO_{FG}/FeO_{AG} = .55						
6-1-1 B						
Zn	110	69	- 41	-37	-1148	- 72
Cu	79	51	- 28	-35	- 784	- 49
Ni	132	66	- 66	-50	-1848	-115
FeO	10.28	10.28	0	0	0	0
MnO	.18	.06	- .12	-67	- 3.4	- .21
Cr	364	326	- 38	-10	-1064	- 66
FeO_{FG}/FeO_{AG} = .61						

Table 13 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/1000cm^{3}glass	Δ g/1000cm^{3}column
6-1-12						
Zn	80	45	- 35	-44	- 980	- 61
Cu	70	34	- 36	-51	-1008	- 63
Ni	68	50	- 18	-27	- 504	- 32
FeO	10.54	10.54	0	0	0	0
MnO	.19	.03	- .16	-84	- 4.5	- .28
Cr						
FeO_{FG}/FeO_{AG} = .51						
8-1-13						
Zn	100	92	- 8	- 8	- 224	- 14
Cu	59	53	- 6	-10	- 168	- 10
Ni	100	131	+ 31	+31	+ 868	+ 54
FeO	7.87	7.87	0	0	0	0
MnO	.23	.17	- .06	-26	- 1.7	- .11
Cr						
FeO_{FG}/FeO_{AG} = .86						
23-1-9 A						
Zn	99	72	- 27	-27	- 756	- 47
Cu	116	76	- 40	-34	-1120	- 70
Ni					0	0
FeO	8.64	8.64	0	0	- 7.8	- .49
MnO	.37	.09	- .28	-76		
Cr						
FeO_{FG}/FeO_{AG} = .73						

Table 13 (cont.)

	FG	AG	AG-FG	Δ %	Δ g/ $1000cm^3$ glass	Δ g/ $1000cm^3$ column
23-1-9 B						
Zn	94	94	0	0	0	0
Cu	74	69	- 5	- 6.8	- 140	- 8.8
Ni	156	87	- 69	-44	-1932	-121
FeO	10.30	10.30	0	0	0	0
MnO	.14	.05	- .09	-64	- 2.5	- .16
Cr						
FeO_{FG}/FeO_{AG} = .73						
24-1-12						
Zn	91	59	- 32	-35	- 896	- 56
Cu	65	38	- 27	-42	- 756	- 47
Ni	110	71	- 39	-35	-1092	- 68
FeO	9.43	9.43	0	0	0	0
MnO	.19	.03	- .16	-84	- 4.5	- .28
Cr	218	207	- 11	- 5.0	- 308	- 19
FeO_{FG}/FeO_{AG} = .54						

Table 13 (cont.)

Average values

	AG-FG	s.d.	Δ %	s.d.	Δ g/ 1000cm^3 glass	s.d.	Δ g/ 1000cm^3 column	s.d.
Zn	- 28	17	- 28	17	- 770	479	- 48	30
Cu	- 23	13	- 29	17	- 632	369	- 39	23
Ni	- 35	40	- 27	31	- 978	1119	- 61	70
FeO	0		0		0		0	
MnO	- .09	.10	- 39	56	- 3	3	- .2	.2
Cr	- 55	51	- 14	14	- 1540	1424	- 96	89

Zn	+ 120 *
Cu	- 30
Ni	-1140
FeO	+ 1
MnO	- .7
Cr	- 330

* from Bohlke (1978), Δ g/ 1000cm^3 basalt

Mn is also lost during the alteration process. In some cases, Fe-Mn oxides have been observed (Honnorez, 1978), but were not found as authigenic minerals in the samples under study. Mn was also found to be lost from the crystalline basalts at this site (Bohlke, 1978).

Table 13 includes Bohlke's (1978) calculations of change in g/1000cm^3 of basalt for comparison. These changes are greater for the glass except for Ni, when comparing the glass with the basalt. However, when the change based on 25% glass present being 25% altered is considered, the effect of the basalt is greater for all species except Cu, where they are comparable.

Zn is the only species where the direction of change differs. Bohlke (1978) reports Zn to be passively accumulated during the alteration of the crystalline basalt. This is not the case for the alteration of the glass, most likely due to differences in the nature of Zn binding in the two phases.

The sediments overlying DSDP Holes 395 and 396 were studied by Varentsov (1978). Site 396 is essentially the same as 396B. The lowest 10 m of sediments lying above the basalt contact show slightly higher heavy metal concentrations than the 30 meters above them. They are associated with Fe and Mn hydroxides in the sediments, a consequence of the hydroxides high sorption capacity, and suggest that they were supplied from hydrothermal solutions ascending from the rift valley of the MAR (Varentsov, 1978). Alteration of the

basalts at site 395, equidistant form the Ridge, but on the west side, has been found to be characteristic of low temperature alteration (Lawrence et al., 1978) (not that of hydrothermal alteration) as has that at site 396B (Bohlke, 1978; Honnorez et al., 1978). The source of Mn in the overlying sediment may be that removed from the basalt, but the Fe is apparently not derived from the basalt. The trace element concentrations associated with the sediments may however be derived from the underlying altered basalt, adsorbed by Fe hydroxides originally deposited by circulating hydrothermal solutions in the sediments.

Discussion

Most of the previous work discussed earlier was concerned with the alteration of crystalline basalts rather than basaltic glasses. Although the glass is, ideally, of the same original composition as the crystalline material comprising the core of a pillow, the alteration processes affect each of them differently due to their different structures and the differences in the incorporation of elemental species into the structures.

Bohlke (1978) found that during the development of brown oxidation zones from fresh, grey, crystalline basalt, Ti, Al, Fe, Ca, Na, Cu and Zn were passively accumulated, and probably Cr. Si, Mg,Ni and probably Mn were removed, and K and H_2O were added. In the alteration of the glasses, Si and Al are mobilized, but redeposited locally in the form of smectites and zeolites. Based on the SiO_2:Al_2O_3 ratios of the deposited phillipsites however, not all the Si lost is redeposited as part of the phillipsite.

Ca is lost from the glasses, and although some is retained in calcite and Ca-rich cements, Ca is released to seawater (Honnorez, 1978). Na is lost from the glass, but more than the amount released is deposited as part of the phillipsites. Na, as well as K, has therefore been removed

from seawater and incorporated into the zeolites.

The effects for Si, Mg, K and Ni are the same for the crystalline and glassy materials, although of different magnitudes, in all cases being more extreme for the glasses. The trends for Si, Mg,Mn and K are generally confirmed in the literature for crystalline basalts (Miyashiro et al., 1969; R.A. Hart, 1970; Melson, 1973; Thompson, 1973; Shido et al., 1974; Humphris and Thompson, 1978a). Effects on Fe, Ca and Ti in these same reports may differ, but may be the result of different bases for calculations of changes.

The situation in regard to trace elements is conflicting, probably due to highly variable localized effects and various methods of reporting (Thompson, 1973; S.R. Hart et al., 1974; Furnes, 1978). Those elements that are either passively accumulated (immobile) or in some cases reported to increase in the alteration of crystalline samples, such as Ti, Al, Fe, Ca and Na, are components of the primary igneous minerals crystallized. Their mobilization will depend on the degree of destruction of the mineral structure in which they are contained, and the pH and Eh conditions during that attack. Where species cannot be solubilized and transported, they tend to remain, and be 'passively accumulated'.

In drawing distinctions between the alteration of the glass and crystalline components, it must also be noted that the discrimination between the altered and fresh materials is very different. The alteration of the glass proceeds to

yield an altered product on the exterior of the body of fresh glass, while the alteration of the crystalline basalts produces a mixed body of the residue of the alteration and the alteration products (clays).

Studies of the alteration of marine basaltic glasses have centered on changes in mineralogy and/or major element chemistry (Marshal, 1961; Bonatti, 1965; Lipman, 1965; Honnorez, 1972; Melson and Thompson, 1973) although Thompson (1973) did examine changes in trace metals. A number of studies (Noble, 1967; Hay and Iijima, 1968; Furnes, 1978) have been concerned with subaerial alteration of volcanic glasses by rain water or ground water. Similar trends have been reported for subaerially altered glasses for the losses of all major oxides, except Fe and K , and for marine alteration (Hay and Iijima, 1968; Thompson, 1973; Furnes 1978).

Subaerial alteration, however, is reported to result in losses of Fe and K. Obviously, fresh water does not provide a source for the accumulation of K, accounting for depleted K. Subaerially altered glass also displays very little authigenic mineral formation other than palagonite, and Al is believed not to be mobile under those alteration conditions (Furnes, 1978). Reported gains at these conditions are the result of removal of other species, rather than additions of Fe.

Similarly, Thompson (1973) and Furnes (1978) reported conflicting trends for Zn, Ni and Cr under marine and

subaerial conditions respectively. Furnes notes, however, that another worker (Pierce, 1970) has found Cr to be concentrated in volcanic tuffs altered in non-marine conditions, but lost by those altered in marine conditions.

The difficulties in comparing the results of these studies lie in both semantics (what is meant by 'change with alteration') and the differences in the environments during alteration. The language problem is that of defining what is considered to be the product of alteration. One gram of glass is not converted to one gram of palagonite, but rather to about one-half that amount. While it may be true that one gram of palagonite may contain more of, say Cu, than a gram of fresh glass, that Cu is the result of accumulation of the contents of more than one gram of glass. It therefore does not represent a removal of Cu from the aqueous system, and may in fact be what remains after the release of some of that species. Thus, the reporting of such studies would be more clear if addressed to the fate of the components of the fresh material, and whether retained in the solid product, released into solution, or redeposited in other phases.

The differences in the chemical environment during alteration, in the cases of subaerial and marine alteration, are immediately apparent when the case of K is considered. In alteration by fresh water, K is removed, while under marine conditions it is accumulated (Hay and Iijima, 1968; Furnes, 1978). Na also displays this effect. In the cases

of the trace metals, a similar problem may account for conflicting results. Transition metal cations may form complexes with species such as sulfate ion, as well as organic complexing agents (Stumm and Morgan, 1970). Where such potential complexing agents are lacking, or present in lower quantities (i.e. fresh waters), these metal species cannot be as effectively transported in solution. The net effect would be that of passive accumulation, and therefore a higher concentration of the specie in the palagonite. Differences in pH conditions may also account for some conflicts and localized variations. Mobilization of Fe and Ti could be caused by acid solutions (Furnes, 1978), but is not apparent in marine low temperature alteration. Furnes also notes that the mobility of Cu, Ni, Cr and Zn is also pH dependent, with greater mobility under acid conditions. Localized differences in pH may account for conflicting trends or differences in degree of alteration, even within a single core.

The alteration of deep sea basalts and basaltic glasses affects the oceanic balances of the elements involved, to the extent that the species released are eventually flushed into the open ocean. Where species are redeposited in the form of authigenic phases within the basalt column, they are not involved in oceanic solution equilibria. Na and K are removed from solution by formation of smectite and phillipsite, contributing to the maintenance of their stable concentration in seawater. Mg flux may vary, depending on the temperature

of alteration (low temperature or hydrothermal), but net results are removal from seawater (Holland, 1978). Some Si appears to escape the basalt column, perhaps contributing to the formation of authigenic phases in the sediment column.

Hydrothermal alteration may be more important in overall oceanic balances of Mg, K and Na than low temperature alteration (Maynard, 1976). Humphris and Thompson (1978a; 1978b) found hydrothermal alteration to be important in the removal of Mg from solution, but found variable trends for Na and K, and found total Fe to increase. Al was not found to be mobilized while Co, Cr, Ni, Cu and Zn were found to be mobilized and in some small degree reprecipitated as sulfide. Massive sulfide mineralization has been reported (Bonatti et al., 1976) as a result of hydrothermal alteration in some locations. The contrast between these conditions and those of low temperature alteration is evident in the difference in mobility of Al, and reprecipitation of some species as sulfide phases.

CONCLUSIONS

Fresh basaltic glasses are the best indicators of initial magma compositions, since crystalline basalts are affected by fractionation and weathering (Hekinian, 1971; Shido et al., 1974; Byerly and Wright, 1978; Kay and Hubbard, 1978). Where the initial magma composition is of primary concern, analyses of the freshest possible glasses are necessary. The importance of obtaining only the freshest glass is evident in the extreme changes displayed by the altered glass, with losses of all major oxides from the fresh glass, except for Fe and Ti, and of all trace metals determined. The contact of fresh and altered glasses is sharp, and the demarcation is apparent under optical examination. Analyses of fresh glass fragments may however be hampered by their small size and the difficulty of removing altered material before analysis, since alteration may proceed along microstructural fractures. Electron microprobe and x-ray milliprobe analyses of clearly defined fresh glasses are perhaps the best method of determining major and trace element contents of these phases.

The marine alteration of fresh glasses results in the release of about one-half the original Si and Al, two-thirds of the Mg and Na, and over 90% of the Ca originally

present, when converted to smectite (or palagonite). Fe and Ti are not mobilized during this alteration, and K is increased 40-fold by removal from seawater. These changes occur during the alteration of glass to palagonite. If the entire solid phase including authigenic cements and zeolites is considered, exchange with seawater results in an overall loss of Ca and Mg, although some is retained. If all the Al released is considered to be redeposited locally, sone Si is also released to seawater, based on the proportions of Si and Al found in the phillipsites. Overall, Na and K are accumulated in the solid phases from seawater.

For the trace metals, over one-quarter of the original Zn, Cu and Ni are lost, about 40% of the Mn, and over 10% of the Cr. Results for individual samples vary from slight gains to extreme losses. This is apparently due to highly variable local pH conditions affecting the alteration.

In general, the alteration of the crystalline basalts shows the same effects for Si, Mg, Mn and K, although the alteration of the glasses is more extreme. Fe, Al, Ti, Na, Ca, Cu, Zn and possibly Cr have been reported as immobile in the crystalline basalts, however (Bohlke, 1978; Honnorez et al., 1978). The differences in the mobility of Al, Na, Ca, Cu, Zn and Cr appear to be a consequence of the difference in their incorporation in the glass and crystalline structures. Where bound in the ordered structures of primary igneous phases, these elements are not readily mobilized during low

temperature alteration. Where they are more loosely contained, in the less orderly glass structure, they are released during the alteration.

Non-marine alteration subjects the glasses to very different condition, resulting in losses of all major oxides including Fe, Ti and K. Enrichments of Cr, Cu and Ni (Furnes 1978) appear to be due to the absence of the species required to solubilize and transport these metals, such as $SO_4^=$ (Stumm and Morgan, 1970). Their increased concentrations in the sediments directly overlying the basalts (Varentsov, 1978) is suggestive of a possible site for the accumulation of these metals following marine alteration, whereas they are retained in the altered glass during non-marine alteration. If these trace metals are transported into the sediment column, other released species may also be deposited there as authigenic phases, rather than in the basalt column.

Estimated fluxes, based on 25% glass in the basalt column, and that glass being 25% altered, show greater losses from the glass for Al, Na and Zn, and a larger gain for K, than for the crystalline materials. This calculation, however, does not consider the authigenic minerals formed. All the Al is apparently retained (Honnorez, 1978), and Na and K accumulated from seawater by the formation of these phases, which also retain some fraction of the released trace metals. The absolute accuracy of these estimates is dependent on the assumptions made on the glass content and extent of altera-

temperature alteration. Where they are more loosely contained, in the less orderly glass structure, they are released during the alteration.

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tion, but they may be easily recalculated for other conditions of glass content or degree of alteration.

The significance of this study is related to how low temperature and hydrothermal alteration affect elemental fluxes, resultant sediment phases, and possibly, deep sea mineral deposits. Oceanic elemental balances are maintained by the interation of sources and sinks for the various species. Deep sea basalts provide a large reservoir due to their coverage of the ocean floor. Those species not retained in the basalt or remaining in solution, may contribute to authigenic phases in the overlying sediment column, such as sulfide deposits in the case of hydrothermal alteration. Quantitative differences in the effects of low and high temperature alteration must also be defined, for a more concise overall view of the net result of seawater - basalt interactions to be developed.

Suggestions for Further Work

The total flux of trace elements resulting from the alteration of basaltic glasses has not been studied in the same manner as that of the major elements (Honnorez, 1978). Such studies could better indicate the final disposition of the trace metals lost during alteration of the glasses - and whether retained in specific authigenic minerals or released into solution. The effect of pH on trace metals during alteration at low temperatures should also be examined, to permit evaluation of the pH of altering fluids by examination of the alteration products.

Further development of the x-ray milliprobe technique used in this study is dependent on the automation of the system, as it currently yields too little information for the time invested. The use of other x-ray tube targets, or a multi-target tube, could expand the range of elements determined, while automation could be used to allow the increased counting times necessary for the use of smaller apertures. Development of a coupled (built-in) optical system would aid in eliminating the difficulties inherent in the site selection procedure that was used, and allow analysis of smaller sample areas.

APPENDIX A

Tabulation of Electron Microprobe Data

Microprobe analyses have been averaged and are tabulated here with an abbreviated label indicating the phase analyzed (see below), the standard deviation, and the number of analyses averaged (in parentheses). Average totals and their standard deviations are also included. 'Others'(Krauskopf, 1967) is the difference between the analyses total and 100%.

Abreviated labels are:

FG	fresh glass
AG	altered glass (smectite, palagonite)
Cal	calcite
Cem	cement (high Ca, high Si)
P	phillipsite
BC	brown microcrystalline
GC	grey microcrystalline
DC	dark crystalline with variolitic outlines
Ol	olivine crystal

Sample numbers including 'A' and 'B' indicate preparations of very different areas of a large sample.

Analyses of adjacent fresh glass - altered glass areas used for calculating changes during alteration appear here as successive FG - AG analyses, in the same order as the normalized analyses in Appendix B.

A number of analyses of crystalline portions of samples are included in the tabulations. However, EMP analyses with the approximately 75 μm spot size used are not well representative of the bulk composition, since the crystallites are on the order of 10-50 μm. Most samples were selected for their fresh and altered glass content, and therefore had little crystalline material.

	FG	(2)	AG	(2)	FG	(2)	AG	(3)
SiO_2	44.21	.76	30.25	2.24	35.37	1.44	34.64	.44
Al_2O_3	14.31	.34	11.79	.97	12.72	.06	10.50	.44
FeO	5.95	.51	10.51	.74	4.63	.76	11.41	.43
MgO	8.01	.34	2.35	.41	7.11	.16	3.37	.14
CaO	7.35	.22	.32	.05	7.41	.53	.12	.01
Na_2O	3.16	.11	2.31	.28	2.70	.06	1.40	.12
K_2O	.09	.02	1.90	.11	.07	.01	2.69	.11
TiO_2	.78	.00	1.26	.06	.78	.07	1.06	.09
Total	83.84	2.24	60.67	1.23	70.79	20.10	65.31	1.24
Others	16.16		39.33		29.21		34.69	

	Cem	(3)	Cem	(2)	Cem	(1)
SiO_2	3.68	1.49	14.51	9.91	13.89	
Al_2O_3	1.57	.84	5.24	4.77	7.11	
FeO	.91	.09	1.00	.24	1.16	
MgO	1.08	.15	1.07	.41	.50	
CaO	36.44	3.75	22.74	2.95	13.27	
Na_2O	.22	.31	2.34	2.21	4.42	
K_2O	.13	.03	1.49	1.29	1.95	
TiO_2	.05	.01	.09	.02	.02	
Total	43.91	1.27	48.47	19.53	42.34	
Others	56.09		51.53		57.66	

Sample 4-1-4 (40-42)

	FG	(3)	AG	(2)
SiO_2	37.15	.44	24.94	2.27
Al_2O_3	14.18	.33	8.98	.27
FeO	6.11	.21	10.29	.08
MgO	7.63	.04	2.41	.11
CaO	8.27	.32	.24	.04
Na_2O	5.22	2.96	1.43	.08
K_2O	.07	.00	1.80	.02
TiO_2	.80	.06	1.23	.02
Total	79.43	2.96	51.29	2.42
Others	20.57		48.71	

Sample 4-2-3 (18-20)

	FG	(2)	AG	(2)	FG	(2)	AG	(2)	Ol	(2)
SiO_2	49.00	.22	40.12	.90	50.44	.16	44.21	.81	39.72	.35
Al_2O_3	15.91	.09	16.94	.38	16.24	.04	11.10	.05	.28	.13
FeO	9.31	.71	14.77	1.02	9.75	.17	15.41	.32	13.57	.48
MgO	8.57	.04	2.26	.09	8.57	.08	3.60	.20	48.59	.12
CaO	11.74	.08	.51	.00	11.31	.12	.73	.17	.31	.01
Na_2O	2.79	.08	2.20	.66	2.98	.09	2.45	.20	.02	.01
K_2O	.10	.00	3.49	.28	.10	.00	3.44	.05	.00	.00
TiO_2	1.30	.00	2.04	.02	1.20	.01	1.78	.01	.06	.02
Total	98.72	.79	82.35	.72	100.58	.52	82.71	.62	102.54	.81
Others	1.28		17.65				17.29			

Sample 4-2-9 (62-64)

	Ol	(4)	BC	(4)	DC	(4)
SiO_2	35.66	.56	43.55	1.49	45.88	.40
Al_2O_3	.05	.06	18.67	2.55	16.30	3.13
FeO	14.23	.44	9.21	1.76	9.07	1.98
MgO	44.96	.81	2.87	.89	6.65	1.67
CaO	.31	.01	13.22	.97	12.76	1.14
Na_2O	.12	.30	3.15	.27	2.72	.24
K_2O	.02	.01	.19	.04	.21	.07
TiO_2	.03	.01	1.12	.39	1.36	.51
Total	95.38	.75	91.98	1.27	94.95	.95
Others	4.62		8.02		5.05	

Sample 5-2-1 (5-7)

	FG	(3)	FG	(4)	FG	(2)	AG	(6)	FG	(4)	AG	(4)
SiO_2	46.29	.90	42.44	.55	44.41	.94	41.74	.85	46.30	2.04	36.98	1.13
Al_2O_3	14.32	.66	13.56	.26	14.33	.34	18.30	2.10	14.60	.15	15.78	.45
FeO	8.70	.48	9.45	.39	9.21	.13	15.98	.46	8.70	.25	15.66	1.47
MgO	8.26	.30	7.79	.15	8.17	.05	2.74	.46	8.12	.19	2.55	.34
CaO	12.20	.09	11.51	.50	11.41	.16	.62	.12	11.93	.18	.62	.18
Na_2O	2.90	.16	2.89	.20	2.84	.05	.52	.10	2.80	.14	1.83	.55
K_2O	.11	.01	.10	.00	.11	.00	2.50	.28	.10	.01	3.32	.31
TiO_2	1.24	.02	1.28	.03	1.23	.02	2.07	.13	1.30	.05	2.12	.20
Total	94.13	1.36	89.02	1.56	91.69	1.66	84.47	1.41	93.85	2.40	78.86	3.03
Others	5.98		10.98		8.29		15.53		6.15		21.14	

Sample 5-2-4 (28-31)

	FG	(2)	AG	(2)	FG	(2)	AG	(2)	FG	(3)	AG	(2)
SiO_2	50.49	.71	39.65	.14	48.47	.16	41.18	.39	51.12	.77	41.52	3.39
Al_2O_3	16.31	.02	17.99	2.57	16.00	.22	15.02	1.22	16.84	.65	17.16	2.68
FeO	9.51	.47	15.59	1.84	9.84	.43	16.05	1.23	9.66	.57	11.15	.76
MgO	8.69	.11	2.19	.48	8.18	.33	2.56	.25	8.38	.13	4.40	2.76
CaO	11.77	.00	.64	.16	11.61	.41	.51	.11	12.05	.46	5.12	4.43
Na_2O	3.19	.02	1.99	.28	2.94	.12	1.60	.26	3.04	.03	1.88	.72
K_2O	.11	.00	3.19	.72	.11	.01	4.11	.00	.11	.00	1.44	.96
TiO_2	1.27	.02	2.10	.26	1.24	.03	2.09	.22	1.27	.03	1.61	.23
Total	101.34	1.18	83.34	.44	98.39	.49	83.12	.48	102.47	2.27	84.28	7.13
Others			16.66		1.61		16.88				15.72	

	P	(5)
SiO_2	54.32	1.84
Al_2O_3	22.57	.44
FeO	1.20	.62
MgO	.27	.18
CaO	.13	.04
Na_2O	7.71	.22
K_2O	6.58	.34
TiO_2	.18	.19
Total	92.96	1.51
Others	7.04	

Sample 6-1-1 (4-7) A

	FG	(4)	AG	(4)	FG	(4)	AG	(4)	GC	(4)
SiO_2	51.16	.63	41.29	1.38	51.55	.31	39.86	1.16	42.16	1.28
Al_2O_3	15.47	.57	15.46	1.75	16.20	.14	14.12	.84	19.26	.19
FeO	9.68	.31	18.07	1.10	9.22	.18	15.70	.16	9.99	.49
MgO	8.09	.18	3.28	.21	8.46	.19	3.04	.12	3.31	.27
CaO	9.27	.51	.66	.13	10.85	.08	.46	.03	11.19	.37
Na_2O	2.83	.03	1.24	.28	2.62	.18	2.67	.31	3.15	.19
K_2O	.10	.00	2.94	.31	.11	.00	2.96	.16	.43	.07
TiO_2	1.20	.08	2.45	.09	1.25	.02	1.97	.07	1.32	.10
Total	97.80	1.79	85.39	3.54	100.26	.52	80.78	.84	90.81	1.96
Others	2.20		14.61				19.22		9.19	

Sample 6-1-1 (4-7) B

	FG	(7)	FG	(4)	AG	(2)	Cem	(2)	BC	(2)
SiO_2	41.18	1.01	39.10	2.80	36.79	4.05	51.74	.67	47.46	.77
Al_2O_3	14.09	.27	13.99	.71	13.23	1.75	23.60	.04	19.83	.61
FeO	8.59	.44	8.36	.73	16.31	.63	1.13	.16	11.58	.32
MgO	8.35	.20	7.99	.28	7.55	4.17	.09	.04	2.82	.21
CaO	11.26	.16	10.22	.47	.54	.00	.16	.02	11.22	.05
Na_2O	2.88	.18	2.35	.53	.91	.06	8.34	2.76	3.45	.07
K_2O	.10	.01	.08	.01	2.53	.44	5.65	.02	.40	.14
TiO_2	1.11	.05	1.30	.03	1.94	.02	.15	.06	1.43	.07
Total	87.56	1.57	83.39	3.22	79.80	5.33	90.86	3.09	98.19	.19
Others	12.44		16.61		20.20		9.14		1.81	

	Ol	(2)	Ol	(2)
SiO_2	25.90	7.22	38.88	.76
Al_2O_3	.87	.73	.11	.08
FeO	44.34	13.10	14.47	.12
MgO	12.84	5.78	47.99	.81
CaO	.39	.07	.30	.02
Na_2O	.51	.10	.00	.00
K_2O	.48	.14	.02	.01
TiO_2	.10	.02	.25	.15
Total	86.07	.03	101.75	1.39
Others	13.93			

Sample 6-1-12 (93-95)

	FG	(2)	AG	(2)	FG	(2)	AG	(2)	AG	(2)
SiO_2	43.24	.34	34.20	1.49	47.75	.22	37.56	.96	35.36	2.28
Al_2O_3	14.98	.35	14.08	.16	15.36	.10	14.22	.10	12.64	1.24
FeO	9.83	.73	16.60	.57	9.00	.16	16.93	.55	14.85	.49
MgO	8.23	.01	2.76	.13	8.62	.07	3.35	.11	3.43	.55
CaO	11.14	.09	.40	.00	10.61	.20	.40	.09	.32	.06
Na_2O	2.73	.14	2.06	.29	2.81	.31	2.56	.59	1.53	.02
K_2O	.11	.00	3.63	.06	.12	.01	3.78	.78	3.56	.54
TiO_2	1.18	.04	2.26	.08	1.17	.04	2.18	.24	1.95	.02
Total	91.44	1.14	75.99	.56	95.44	.89	80.96	1.86	73.63	1.54
Others	8.56		24.01		4.56		18.04		26.37	

	Cem	(2)	Cem	(2)
SiO_2	41.03	7.00	52.59	.38
Al_2O_3	16.81	1.76	20.90	.29
FeO	.59	.06	.65	.12
MgO	.18	.04	.04	.03
CaO	.06	.00	.00	.00
Na_2O	6.11	.13	7.78	.56
K_2O	6.02	.24	6.97	.09
TiO_2	.15	.10	.04	.00
Total	70.95	9.02	88.67	.14
Others	29.05		11.33	

Sample 6-1-14 (107-112)

	GC	(4)	DC	(5)
SiO_2	37.01	5.76	42.95	.40
Al_2O_3	15.00	.71	16.53	.76
FeO	5.20	.22	5.59	.44
MgO	4.07	2.22	4.42	1.00
CaO	6.16	.36	6.16	.44
Na_2O	3.48	.29	3.57	.13
K_2O	.12	.05	.08	.01
TiO_2	.67	.04	.66	.09
Total	71.71	7.08	80.00	.75
Others	28.29		20.00	

Sample 7-1-12 (142-144)

	Cal	(2)	GC	(4)	BC	(4)
SiO_2	.04	.04	43.23	3.15	40.80	.90
Al_2O_3	.02	.02	19.73	4.84	15.45	3.45
FeO	.75	.16	8.05	2.28	6.98	2.38
MgO	2.34	.18	3.06	1.75	3.50	2.58
CaO	47.41	.82	11.36	.71	11.70	.75
Na_2O	.00	.00	3.81	.25	3.48	.60
K_2O	.00	.00	.35	.16	.30	.11
TiO_2	.02	.01	1.08	.48	1.06	.35
Total	50.58	.43	90.65	3.54	83.17	.96
Others	49.59		9.35		16.83	

Sample 7-2-9 (97-102)

	P	(2)	P	(3)	Cal	(2)	DC	(3)	BC	(3)
SiO_2	56.14	2.99	58.29	6.45	.06	.04	50.51	.77	46.50	3.06
Al_2O_3	19.84	1.82	21.84	2.37	.00	.00	18.57	1.01	19.59	1.61
FeO	1.76	1.23	.51	.07	.73	.11	9.86	.62	10.21	2.36
MgO	2.61	2.61	.06	.06	2.87	.23	8.56	2.19	3.87	.99
CaO	.20	.16	.09	.02	56.66	.36	10.73	1.61	12.68	.97
Na_2O	6.16	3.98	4.73	1.58	.00	.00	3.18	1.42	3.37	.45
K_2O	4.60	.92	1.77	.69	.01	.00	.13	.06	.15	.05
TiO_2	.04	.03	.02	.01	.02	.00	.89	.38	1.07	.27
Total	91.35	5.69	87.31	9.67	60.35	.42	102.43	1.67	97.44	1.68
Others	8.65				39.65				2.56	

Sample 8-1-13 (118-120)

	FG	(3)	DC	(2)
SiO_2	42.24	1.78	45.73	.02
Al_2O_3	14.67	1.56	15.90	.57
FeO	9.12	.72	8.89	.01
MgO	6.51	1.43	7.05	.50
CaO	10.70	.02	11.74	.30
Na_2O	3.13	.16	2.99	.05
K_2O	.12	.03	.13	.02
TiO_2	1.32	.07	1.46	.05
Total	87.81	2.76	93.89	.42
Others	12.19		6.11	

Sample 23-1-9

	FG	(3)	AG	(3)	FG	(7)	AG	(5)	FG	(2)	AG	(2)
SiO_2	43.72	.34	37.61	.56	50.26	1.22	39.78	2.79	49.74	.42	43.26	1.39
Al_2O_3	15.40	.32	13.80	2.15	17.01	.32	12.79	1.67	17.12	.33	13.35	.77
FeO	7.94	.47	12.62	.90	10.39	.64	16.75	1.07	8.81	.23	13.68	.56
MgO	7.90	.17	9.51	3.18	8.03	.30	6.92	1.30	7.56	.11	8.49	.04
CaO	10.08	.17	1.40	1.40	10.17	.83	1.13	.94	12.86	.16	7.32	1.89
Na_2O	3.33	.30	2.03	.36	3.12	.13	2.77	.48	2.84	.05	2.38	.01
K_2O	.16	.01	1.49	.65	.19	.02	2.28	.29	.17	.01	1.26	.49
TiO_2	1.24	.01	1.92	.15	1.32	.06	2.45	.23	1.43	.03	1.97	.13
Total	89.77	1.36	80.38	.32	100.49	2.55	84.87	2.28	100.53	.51	91.71	2.88
Others	10.23		19.62				15.13				8.29	

	P	(4)	P	(3)
SiO_2	54.85	1.34	56.02	.64
Al_2O_3	21.85	.18	22.20	.14
FeO	.51	.14	.75	.03
MgO	.00	.00	.04	.03
CaO	.00	.00	.04	.03
Na_2O	9.45	.43	7.53	.30
K_2O	5.50	.13	6.84	.25
TiO_2	.02	.01	.02	.00
Total	92.18	1.12	93.44	.81
Others	7.82		6.56	

Sample 24-1-12 (74-76)

	FG	(3)	AG	(2)	FG	(4)	AG	(2)	FG	(5)	AG	(3)
SiO_2	40.65	1.34	34.74	.31	45.19	.61	35.67	.22	47.12	.43	38.46	.86
Al_2O_3	15.07	.45	9.67	.19	15.79	.30	10.08	.10	16.56	.64	10.55	.48
FeO	8.49	.21	15.11	.04	9.23	.73	17.01	.10	9.51	.38	16.80	.93
MgO	7.89	.17	4.89	.10	9.39	1.36	4.35	.27	7.62	.19	2.95	2.09
CaO	11.36	.64	.50	.02	12.55	.34	.40	.00	12.87	.25	.46	.05
Na_2O	3.30	.15	2.47	.55	3.05	.11	1.34	.05	3.14	.16	2.21	.26
K_2O	.16	.00	3.00	.11	.15	.02	3.95	.40	.18	.02	3.37	.21
TiO_2	1.41	.07	2.44	.07	1.23	.10	2.62	.19	1.37	.06	2.43	.01
Total	88.33	2.20	72.82	.98	96.58	1.66	75.52	.04	98.37	.57	77.23	2.23
Others	11.67		27.18		3.42		24.58		1.63		22.77	

	P	(2)	P	(2)	P	(3)	Ol	(3)	GC	(2)
SiO_2	45.06	3.39	49.89	.99	50.16	1.13	34.73	.55	49.17	.73
Al_2O_3	18.70	1.41	20.75	.24	20.61	.28	.06	.05	18.28	.63
FeO	.46	.15	.40	.09	.87	.06	13.50	.75	9.09	.29
MgO	.01	.01	.01	.01	.02	.03	46.34	.30	5.16	.09
CaO	.02	.00	.08	.01	.03	.03	.33	.01	12.09	.47
Na_2O	14.58	2.09	8.11	.34	7.21	.69	.07	.10	3.28	.08
K_2O	6.06	.60	6.06	.02	7.12	.43	.00	.00	.24	.02
TiO_2	.01	.00	.00	.00	.03	.01	.01	.01	1.46	.09
Total	84.86	3.21	85.30	1.21	86.33	.33	95.04	.67	98.77	1.59
Others	15.10		14.70		13.95		4.96		1.23	

APPENDIX B

Tabulation of Normalized Fresh and Altered Glass EMP Data

Microprobe analyses of paired (adjacent) fresh and altered glass areas have normalized to 100% and are tabulated here. The tables also include a calculation of the % change between the two phases as

$$\Delta\ \% = ((AG-FG)/FG) \times 100\% \ .$$

This calculation for 'others' is based on the 'others' figures in Appendix A, since this component is removed by normalization to 100% to arrive at a weight percent total analysis. The FG - AG pairs appear in the same order as tabulated in Appendix A.

Sample 4-1-4 (40-42)

	FG	AG	FG	AG	FG	AG
SiO_2	52.61	49.91	49.87	53.00	46.81	48.63
Al_2O_3	17.03	19.45	17.94	16.07	17.87	17.51
FeO	7.08	17.34	6.53	17.46	7.70	20.07
MgO	9.53	3.88	10.03	5.16	9.61	4.70
CaO	8.75	.53	10.45	.18	10.42	.47
Na_2O	3.76	3.81	3.81	2.14	6.58	2.79
K_2O	.11	3.14	.10	4.12	.09	3.51
TiO_2	.93	2.08	1.10	1.62	1.01	2.40
Total	99.77	100.11	99.81	99.92	100.08	100.02

	Δ%	Δ%	Δ%
SiO_2	- 5	+ 6	+ 4
Al_2O_3	+ 14	- 10	- 2
FeO	+ 145	+ 167	+ 161
MgO	- 59	- 49	- 51
CaO	- 94	- 98	- 95
Na_2O	+ 1	- 44	- 58
K_2O	+2755	+4020	+3800
TiO_2	+ 124	+ 47	+ 138
Others	+ 143	+ 19	+ 137

Sample 4-2-3 (19-20)

	FG	AG	FG	AG
SiO_2	49.49	48.55	50.44	53.49
Al_2O_3	16.07	20.50	16.24	13.43
FeO	9.40	17.87	9.75	18.65
MgO	8.66	2.73	8.57	4.36
CaO	11.86	.62	11.31	.88
Na_2O	2.82	2.66	2.98	2.96
K_2O	.10	4.22	.10	4.16
TiO_2	1.31	2.47	1.20	2.15
Total	99.71	99.64	100.58	100.08

	Δ %	Δ %
SiO_2	- 2	+ 6
Al_2O_3	+ 28	- 17
FeO	+ 90	+ 91
MgO	- 68	- 49
CaO	- 95	- 92
Na_2O	- 6	- 1
K_2O	+4120	+4060
TiO_2	+ 89	+ 79
Others	+1279	

Sample 5-2-1 (5-7)

	FG	AG	FG	AG
SiO_2	49.07	49.25	49.54	46.96
Al_2O_3	15.18	21.59	15.62	20.04
FeO	9.22	18.86	9.31	19.89
MgO	8.76	3.23	8.69	3.24
CaO	12.93	.73	12.77	.79
Na_2O	3.07	.61	3.00	2.32
K_2O	.12	2.95	.11	4.22
TiO_2	1.31	2.44	1.39	2.69
Total	99.66	99.67	100.42	100.15

	Δ %	Δ %
SiO_2	+ 1	- 5
Al_2O_3	+ 42	+ 28
FeO	+ 105	+ 114
MgO	- 63	- 63
CaO	- 94	- 94
Na_2O	- 80	- 23
K_2O	+2358	+3736
TiO_2	+ 86	+ 94
Others	+ 160	+ 244

Sample 5-2-4 (28-31)

	FG	AG	FG	AG	FG	AG
SiO_2	50.49	47.58	49.44	49.42	51.12	49.41
Al_2O_3	16.31	21.59	16.32	18.02	16.84	20.42
FeO	9.51	18.71	10.04	19.26	9.66	13.27
MgO	8.69	2.63	8.34	3.07	8.38	5.24
CaO	11.77	.77	11.84	.61	12.05	6.09
Na_2O	3.19	2.39	3.00	1.92	3.04	2.24
K_2O	.11	3.83	.11	4.93	.11	1.71
TiO_2	1.27	2.52	1.26	2.51	1.27	1.92
Total	101.34	100.01	100.36	99.74	102.47	100.29

	Δ %	Δ %	Δ %
SiO_2	- 6	- 0	- 3
Al_2O_3	+ 32	+ 10	+ 21
FeO	+ 97	+ 92	+ 37
MgO	- 70	- 63	- 37
CaO	- 93	- 95	- 49
Na_2O	- 25	- 36	- 26
K_2O	+3382	+4382	+1455
TiO_2	+ 98	+ 99	+ 51
Others		+ 948	

Samples 6-1-1 (4-7) A & B

	FG	AG	FG	AG	FG	AG
SiO_2	52.18	48.31	51.55	49.43	46.92	45.99
Al_2O_3	15.78	18.09	16.20	17.51	16.79	16.54
FeO	9.87	21.14	9.22	19.47	10.03	20.39
MgO	8.25	3.84	8.46	3.77	9.59	9.44
CaO	9.46	.77	10.85	.57	12.26	.68
Na_2O	2.89	1.45	2.62	3.31	2.82	1.14
K_2O	.10	3.44	.11	3.67	.10	3.16
TiO_2	1.22	2.87	1.25	2.44	1.56	2.43
Total	99.76	99.91	100.26	100.17	100.07	99.75

	Δ %	Δ %	Δ %
SiO_2	- 7	- 4	- 2
Al_2O_3	+ 15	+ 8	- 1
FeO	+ 114	+ 111	+ 103
MgO	- 53	- 55	- 2
CaO	- 92	- 95	- 94
Na_2O	- 50	+ 26	- 60
K_2O	+3340	+3236	+3060
TiO_2	+ 135	+ 95	+ 56
Others	+ 564		+ 22

Sample 6-1-12 (93-95)

	FG	AG	FG	AG	AG
SiO_2	47.13	45.14	50.14	46.57	48.09
Al_2O_3	16.33	18.59	16.13	17.63	17.19
FeO	10.71	21.91	9.45	20.99	20.20
MgO	8.97	3.64	9.05	4.15	4.66
CaO	12.14	.53	11.14	.50	.44
Na_2O	2.98	2.72	2.95	3.17	2.08
K_2O	.12	4.79	.13	4.69	4.84
TiO_2	1.29	2.98	1.23	2.70	2.65
Total	99.67	100.31	100.21	100.39	100.14

	Δ %	Δ %	Δ %	
SiO_2	- 4	- 7	- 4	
Al_2O_3	+ 14	+ 9	+ 7	
FeO	+ 105	+ 122	+ 114	
MgO	- 59	- 54	- 49	
CaO	- 96	- 96	- 96	
Na_2O	- 9	+ 7	- 29	
K_2O	+3892	+3508	+3623	
TiO_2	+ 131	+ 120	+ 115	
Others	+ 180	+ 296	+ 478	(2 distinct AG fragments)

Sample 23-1-9

	FG	AG	FG	AG	FG	AG
SiO_2	48.53	46.64	50.26	46.94	49.74	47.15
Al_2O_3	17.09	17.11	17.01	15.09	17.12	14.55
FeO	8.81	15.65	10.39	19.77	8.81	14.91
MgO	8.77	11.79	8.03	8.17	7.56	9.25
CaO	11.19	1.74	10.17	1.33	12.86	7.98
Na_2O	3.70	2.52	3.12	3.27	2.84	2.59
K_2O	.18	1.85	.19	2.69	.17	1.37
TiO_2	1.38	2.38	1.32	2.89	1.43	2.15
Total	99.64	99.67	100.49	100.15	100.53	99.96

	Δ %	Δ %	Δ %
SiO_2	- 4	- 7	- 5
Al_2O_3	+ 0	- 11	- 15
FeO	+ 78	+ 90	+ 69
MgO	+ 34	+ 2	+ 22
CaO	- 84	- 87	- 38
Na_2O	- 32	+ 5	- 9
K_2O	+ 927	+1316	+ 706
TiO_2	+ 72	+ 120	+ 50
Others	+ 92		

Sample 24-1-12 (74-76)

	FG	AG	FG	AG	FG	AG
SiO_2	45.93	47.59	47.00	47.44	48.06	49.61
Al_2O_3	17.03	13.25	16.42	13.41	16.89	13.61
FeO	9.59	20.70	9.60	22.62	9.70	21.67
MgO	8.92	6.70	9.77	5.79	7.77	3.81
CaO	12.84	.69	13.05	.53	13.13	.59
Na_2O	3.73	3.38	3.17	1.78	3.20	2.85
K_2O	.18	4.11	.16	5.25	.18	4.35
TiO_2	1.59	3.34	1.28	3.48	1.40	3.13
Total	99.81	99.76	100.44	100.31	100.34	99.63

	Δ %	Δ %	Δ %
SiO_2	+ 4	+ 1	+ 3
Al_2O_3	- 22	- 18	- 19
FeO	+ 116	+ 136	+ 123
MgO	- 25	- 41	- 51
CaO	- 95	- 96	- 96
Na_2O	- 9	- 44	- 11
K_2O	+2183	+3181	+2317
TiO_2	+ 110	+ 172	+ 124
Others	+ 133	+ 619	+1297

APPENDIX C

Tabulation of XMP Data and % Change Calculations

Averages of x-ray milliprobe data are tabulated here with an abbreviated label indicating the phase analyzed (see key in Appendix A), the standard deviation, and the number of analyses averaged (in parentheses). Calculations of the % change between the paired FG - AG analyses are also included here, as in Appendix B. Sample numbers including 'A' and 'B' indicate preparations of very different areas of a large sample.

Average r and σ values for the fits from the XRF-4 program are listed below, with the standard deviation. For samples where not all elements are reported, this may be because of inclusion of some earlier runs where not all were determined, rejection of a single element due to poor fit of the standards, or for Cr, the lack of data for those analyses made using the 100 μm aperture.

	r	s.d.	σ	s.d.
Zn	.971	.021	18	7
Cu	.976	.035	11	5
Ni	.967	.033	18	9
FeO	.988	.001	.50	.20
MnO	.989	.008	.02	.01
Cr	.967	.037	46	16

Even when the number of points fitted is only 6, the required r value for the 99% confidence limit is .917, and for the 99.9% limit is .974 (Hinchen, 1969). The r values for the runs used always exceeded the value for the 99% limit, and usually that for the 99.9% limit, using 8 to 10 points.

Zn, Cu, Ni are reported in ppm ; FeO and MnO as %.

Sample 4-1-4 (40-42)

	FG	(2)	AG	(9)	Cem	(3)
Zn	94	1	100	6	89	11
Cu	66	4	107	35	97	41
Ni	131	11	65	29	24	*
FeO	7.35	.04	18.08	2.00	.30	.16
MnO	.17	.01	.09	.06	.04	.02
Cr						

	Δ %
Zn	+ 6
Cu	+ 62
Ni	- 50
FeO	+146
MnO	- 47
Cr	

* 1 determination

Sample 4-2-3 (18-20)

	FG	(2)	AG	(6)
Zn	88	0	89	15
Cu	60	6	56	4
Ni	122	9	105	28
FeO	8.51	.76	14.90	2.43
MnO	.15	.01	.19	.18
Cr	95	28	181	55

	Δ %
Zn	+ 1
Cu	- 7
Ni	- 14
FeO	+ 75
MnO	+ 27
Cr	+ 91

Sample 4-2-9 (62-64)

	Ol	(5)	BC+DC	(10)
Zn	74	19	104	6
Cu	57	4	66	3
Ni	610	97	114	47
FeO	16.28	2.18	9.53	1.10
MnO	.25	.03	.15	.02
Cr	329	19	379	57

Sample 5-2-1 (5-7)

	FG	(5)	FG	(5)	FG	(2)	AG	(3)
Zn	115	2	113	2	116	1	117	3
Cu	84	3	83	2	147	0	157	14
Ni	137	7	151	41				
FeO	9.47	.22	9.74	.57	10.18	.83	13.76	1.03
MnO	.17	.02	.24	.13	.26	.08	.15	.05
Cr	322	16	331	78				

	Δ %
Zn	+ 1
Cu	+ 7
Ni	
FeO	+ 35
MnO	- 42
Cr	

Sample 5-2-1 (5-7) (cont.)

	FG	(3)	AG	(2)	FG	(2)	AG	(2)
Zn	106	2	104	1	86	5	90	2
Cu	75	1	78	1	70	2	80	4
Ni	139	18	182	51	84	16	100	10
FeO	9.34	.12	10.87	.06	9.75	.02	10.48	.04
MnO	.18	.01	.23	.09	.22	.01	.15	.01
Cr	303	16	276	47				

	Δ %	Δ %
Zn	- 2	+ 5
Cu	+ 4	+ 14
Ni	+ 31	+ 19
FeO	+ 16	+ 7
MnO	+ 28	- 32
Cr	- 9	

Sample 5-2-4 (28-31)

	FG	(2)	AG	(2)	FG	(3)	AG	(2)
Zn	90	32	103	9	105	11	116	12
Cu	64	4	55	2	66	3	66	2
Ni	64	30	75	2	123	33	147	11
FeO	12.18	1.47	15.46	5.10	9.25	.90	16.92	.83
MnO	.20	.04	.21	.13	.20	.04	.18	.02
Cr	422	4	346	18				

	Δ %	Δ %
Zn	+ 14	+ 10
Cu	- 14	0
Ni	+ 17	+ 20
FeO	+ 27	+ 83
MnO	+ 5	- 10
Cr	- 18	

Sample 5-2-4 (28-31) (cont.)

	Cem	(1)	P	(1)
Zn	83		118	
Cu	63		70	
Ni	105		123	
FeO	2.53		3.28	
MnO	.23		.27	
Cr	320			

Sample 6-1-1 (4-7) A

	FG	(7)	AG	(2)	BC	(3)
Zn	109	8	102	2	106	5
Cu	78	7	74	4	72	2
Ni	141	10	132	1	172	29
FeO	9.72	.52	17.83	1.76	9.83	1.85
MnO	.18	.02	.06	.04	.23	.10
Cr	363	41	530	55	329	49

	Δ %
Zn	- 6
Cu	- 5
Ni	- 6
FeO	+ 83
MnO	- 67
Cr	+ 46

Sample 6-1-1 (4-7) B

	FG	(4)	AG	(4)	GC	(2)
Zn	110	2	112	4	113	1
Cu	79	1	83	1	78	1
Ni	132	4	108	20	148	20
FeO	10.28	1.05	16.79	1.05	12.90	1.39
MnO	.18	.01	.09	.03	.17	.01
Cr	364	48	532	83	527	39

	Δ %
Zn	+ 2
Cu	+ 5
Ni	- 18
FeO	+ 63
MnO	- 50
Cr	+ 46

Sample 6-1-12 (93-95)

	FG	(2)	AG	(3)	Cem	(2)
Zn	80	6	89	24	70	4
Cu	70	1	66	2	62	1
Ni	68	18	99	20	92	2
FeO	10.54	.15	20.67	.80	0	0
MnO	.19	.08	.06	.03	.07	.02
Cr						

	Δ %
Zn	+ 11
Cu	- 6
Ni	+ 46
FeO	+ 96
MnO	- 68
Cr	

Sample 6-1-14 (107-112)

	BC	(14)	BC*	(2)
Zn	112	5	1632	212
Cu	70	3	9887	1236
Ni	84	8	104	2
FeO	9.39	1.08	8.82	.39
MnO	.12	.01	.11	.01
Cr	392	30	312	16

*dark interstitial fillings

Sample 7-1-12 (142-144)

	BC+GC	(6)	Cal	(3)
Zn	118	13	121	12
Cu	72	4	90	9
Ni	124	60	159	49
FeO	8.25	1.76	.61	.62
MnO	.24	.10	.21	.14
Cr	311	38	113	20

Sample 7-2-9 (97-102)

	BC	(14)	P	(3)
Zn	95	15	69	26
Cu	70	3	73	8
Ni	127	39	52	21
FeO	9.65	.72	.09	.11
MnO	.20	.07	.04	.02
Cr	322	74	121	122

Sample 8-1-13 (118-120)

	FG	(2)	AG (1)	BC	(2)	GC	(2)
Zn	100	16	107	106	11	90	15
Cu	59	1	61	68	1	59	1
Ni	100	17	152	68	11	110	16
FeO	7.87	.10	9.15	9.00	.22	7.62	.41
MnO	.23	.02	.20	.18	.01	.19	.05
Cr							

	Δ %
Zn	+ 7
Cu	+ 3
Ni	+ 52
FeO	+ 16
MnO	- 13
Cr	

	FG	(3)	AG	(2)	FG	(2)	AG	(3)
Zn	99	1	98	4	94	18	129	10
Cu	116	3	104	8	74	7	95	1
Ni					156	51	119	2
FeO	8.64	.84	11.81	.02	10.30	.07	14.11	1.84
MnO	.37	.26	.12	.06	.14	.03	.07	.06
Cr								

Sample 23-1-9

	Δ %	Δ %
Zn	- 1	+ 37
Cu	- 10	+ 28
Ni		- 24
FeO		+ 37
MnO	+ 37	- 50
Cr	- 68	

Sample 24-1-12 (74-76)

	FG	(13)	AG	(3)	P	(2)
Zn	91	37	108	47	110	14
Cu	65	12	70	15	91	3
Ni	110	34	130	20	78	32
FeO	9.43	1.43	17.35	3.67	2.94	2.94
MnO	.19	.04	.05	.03	.05	.05
Cr	218	153 *	382**		350	2

	Δ %
Zn	+ 19
Cu	+ 8
Ni	+ 18
FeO	+ 84
MnO	- 74
Cr	+ 75

* (n=7) ** (n=1)

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